TEXTILE RESEARCH JOURNAL

Publication of

TEXTILE RESEARCH INSTITUTE

VOLUME 31 JUNE 1961 NUMBER 6

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TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Manuscripts and communications should be sent to the Publications Department, P.O. Box 625, Princeton, N. J.

Second-class postage paid at Lancaster, Pa.

Subscription rates: $25.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $2.50 each.

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Comparison of Ultraviolet Light Absorbers for Protection of Wool Against Yellowing

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Abstract

The use of ultraviolet light absorbers to protect wool against yellowing by ultraviolet light is reported. The substances tested were evaluated by measuring the change in the reflectance of treated and untreated wool cloth, after irradiation with several light sources. Great differences were observed in the protection obtained from substances having similar strong absorption spectra in the ultraviolet. Substituted benzophenones were effective protective agents, but the method of application is important. The best results were obtained with sulfonated substituted benzophenones, applied from hot, aqueous solutions having a pH of about 1.5. The protection afforded by this treatment was partly retained after washing with soap and water. Unsulfonated substituted benzophenones having about the same absorption characteristics, applied from alcoholic solutions, were much less effective. The implications of these results are briefly discussed.

Introduction

Yellowing by light presents problems to manufacturers and users of fabrics made from both natural and synthetic fibers. These problems are of more concern where the fiber is used in the production of pastel or other light colored textile products. Fashion trends that favor the use of light colored fabrics make the matter one of increasing importance.

There are at least three basic approaches to the problem of protecting wool fibers from damage by light. One approach is to employ a reagent that reacts chemically with the group or groups in the fiber that are sensitive to the irradiation, to produce a chemically modified fiber more stable to degradation by light. This requires a knowledge of the light-sensitive groups in the fiber and some information regarding the nature of the chemical reactions involved in the degradation. Since this information is not known, it is not feasible to use this approach. In the second approach an endeavor is made to coat the fiber with a covering that is opaque to the damaging radiation. A third, and closely related approach involves the application of a substance that will absorb the damaging radiation and dissipate its energy in some innocuous form. Several substituted 2-hydroxybenzophenones that function in the latter manner have been developed and marketed in recent years. A discussion of the properties of these materials, descriptions of their use in the stabilization of plastic and resinous films and sheets, and a discussion of the possible application of these ultraviolet light absorbers to textile products was presented by Gantz and Sumner [4]. Coleman

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and Peacock [2] have also discussed the effects of ultraviolet and visible light on a variety of natural and synthetic materials and have described the prevention or inhibition of the photodegradation of dyed cotton, and of the dyes on cotton, by interposing an ultraviolet-absorbing screen between the dyed fabric and the light source, and measuring the rate of fading of the dye. The ultraviolet-light-absorbing screen consisted of cellulose acetate film containing about 0.5% of a substituted 2-hydroxybenzophenone. In a brief discussion of the application of ultraviolet light absorbers to textiles, Coleman and Peacock [2] state, "The application of ultraviolet absorbers to textiles has not yet been explored very thoroughly," and in conclusion they state, "The ultraviolet light is an important cause in the fading of practically all dyes, in the weakening of fibers and fabrics, and in the photodegradation of many other substances. Ultraviolet absorbers have been applied to many substances and have been successful in many cases in neutralizing the destructive attack of ultraviolet light. However, many more studies on their application to fibers will be necessary before maximum effectiveness can be attained."

The results of our work on the application of ultraviolet light absorbers to minimize yellowing of wool are presented in this paper. Our studies were confined to the problem of yellowing. Other degradative changes accompany the yellowing of wool exposed to ultraviolet light. Extensive radiation of untreated wool results in the wool becoming gummy on the exposed surface and in the development of acidity, as noted in aqueous extracts of the wool. Severely irradiated wool retains only a small fraction of the mechanical strength of unirradiated wool. A limited number of experiments were made on dyed wools to ascertain if the fading of the dye, on exposure to light, could be minimized or eliminated by adding an ultraviolet light absorber to the dye bath at the time of application of the dye. Although some protection against fading was obtained with one or two dyes, this aspect of the problem was considered to be beyond the scope of the work reported here and was not pursued further.

Experimental Procedure

Materials

Wool. The wool, in the form of cloth, was obtained from two commercial sources. It was purchased as unbleached wool flannel that had received no chemical treatment other than the usual soap and soda scour of the raw wool. Before use, the flannel was extracted with carbon tetrachloride in a Soxhlet extractor and washed with water (50° C.) to remove residual oil and grease.

Ultraviolet absorbers. Most of the substances used for treating the wool before exposure to irradiation were obtained from commercial sources. Others were prepared in this laboratory. A portion of the 2-hydroxy-4-methoxy-4′-*t*-butylbenzophenone (Compound III) was prepared in this laboratory by the Fries rearrangement of 3-methoxyphenyl-*t*-butylbenzoate. Its melting point, the melting point of a mixture of this substance and some furnished by the American Cyanamid Company, and the melting point of the latter substance alone, were all identical. This material was sulfonated at 50° with sulfuric acid containing 5% excess sulfur trioxide. The sulfonation product was found to be 2-hydroxy-4-methoxy-4′-*t*-butylbenzophenone-5-sodium sulfonate (Compound VI). Details of the preparation and proof of structure will be published elsewhere. It is of interest to note that VI is much less soluble in water than 2-hydroxy-4-methoxy-benzophenone-5-sodium sulfonate (Compound II). 2,4-Dihydroxybenzophenone-2′-ammonium sulfonate (Compound IV) was prepared by Blackshear's modification [1] of the method first described by Remsen and Hayes [9]. The substance was recrystallized alternately from 50% aqueous alcohol and from water, using decolorizing carbon with the recrystallization from water. Six or seven recrystallizations were required to obtain a colorless product. Diphenylmethane and 5,5′-dichloro-2,2′dihydroxydiphenylmethane were sulfonated in chloroform solution with chlorosulfonic acid, by the method of Wedekind and Schlenk [11], to obtain the monosulfonic acid. The disulfonate of diphenylmethane was prepared by Doer's method [3], using a mixture of sulfuric and fuming sulfuric acids, at 97°; these products were isolated as the sodium salts. Xanthpinnacol was prepared by the method of Gomberg and Bachmann [6].

Method of Treatment

In our first experiments, the ultraviolet light absorbers were applied by placing the wool cloth in a solution of the substance. Where solubility permitted, proportions were 0.25 g. substance and 7 ml. ethanol for 1.5 g. wool. Under these conditions the

solution was essentially all absorbed by the cloth; the solvent was permitted to evaporate; little or no crust remained in the dish. This technique will hereafter be referred to as evaporation impregnation. The material usually adhered firmly to the dry wool, which was brushed lightly to remove loose material adhering to the surface, and exposed to a lamp, as described below. In subsequent work, the ultraviolet light absorbers were sulfonated to give water-soluble products having the affinity of dyes, and these were applied by exhaustion onto the wool from hot aqueous solution, using various temperatures, times, and additives (salts) in the solution. The latter procedure was the more effective and was used in most of this work.

Measurement of Extent of Yellowing

The change in the reflectance of wool, after standardized exposure to the radiation from one of several light sources, was used as a measure of the effectiveness of the protection provided by the treatment that preceded the irradiation. The reflectance of the cloth was measured on a Photovolt[3] reflectometer; this instrument has a circular photocell surrounding the incident beam, thus avoiding orientation effects due to the weave of cloth samples. Rotation of the samples did not influence the reflectometer reading. Spectrophotometric studies of the yellowing showed the color to be due to nonspecific absorption in the shorter wavelengths; the differences were accentuated by using a blue glass filter having maximum transmission at 430 mμ. The results correlated well with visual comparison of gradations of color. For screening operations, the cloth samples were stapled to a card and exposed to the source of radiation; the reflectance was measured after periods of approximately 24 and 48 hr. The treated samples were invariably accompanied, during exposure, by untreated cloth as controls. For more rigid comparison, i.e., the results reported in Figures 1–4, round metal boxes were used to hold the samples for the measurement of reflectance and for reproducible placement for exposure. The boxes were approximately 50 mm. in diameter and 18 mm. deep, and holes approximately 22 mm. in diameter had been cut in the bottoms. The cloth was placed smoothly across the bottom of the box and held firmly in place by a metal ring. For measurement of reflectance, each box was placed on top of the measuring head of the reflectometer, and the reflectance was read to the nearest ½ scale division; each division represented 1% reflectance. For irradiation under the fluorescent sunlamp and the germicidal lamp (see below) the boxes holding the cloth were placed in a frame with fixed positions for the boxes. Reflectance measurements were made after periods of 6, 24, 48, 96, and 168 hr. The positions of the metal boxes were rotated after each exposure to avoid radiation gradients in the lamp, major gradients being avoided by excluding the filamentary zones. The distance from the lamp to the surface of the cloth was about 20 mm. Irradiation under these conditions resulted in a cloth temperature of approximately 32° C.

Several factors may influence the reproducibility of the results reported, but these factors were minimized or eliminated by conducting blank or control experiments on untreated cloth simultaneously with the experiments on treated cloth. Control cloths, treated under identical conditions, but with no ultraviolet light absorber present, gave results similar to untreated controls. Exposure of the untreated cloth with the sample compensated for variation in yellowing due to aging of the lamp or day-to-day changes in humidity or line voltage. Lack of uniformity of the cloth resulted in variations of ½ to 1½ scale units (0.5% to 1.5% reflectance) but this variation was largely eliminated by the use of controls, as indicated above. The reflectometer scale was read to 0.5 unit, and was reproducible to this degree by checking the instrument against a reflectance standard before and after each reflectance reading.

Light Sources

Four light sources were used: a 15-watt germicidal lamp, emitting three fourths of its light at 253.7 mμ; a 20-watt fluorescent sunlamp, having peak emission at about 310 mμ; a 275-watt type RS sunlamp (combining incandescent and high pressure mercury arc); and a "black light" fluorescent lamp emitting in the longest wavelength ultraviolet (peak 365 mμ). The type RS lamp was not particularly effective in yellowing the wool and the interpretation of the results obtained was complicated by the possible effects of the heat generated by the lamp; for these reasons, use of the lamp was limited, and the results obtained with it are not reported. The germicidal

[3] Mention of specific products and equipment is for purposes of identification, and does not imply endorsement by the U. S. Department of Agriculture.

TABLE I. Treatment of Wool with Various Ultraviolet Light Absorbers, and the Protection Against Yellowing Thereby Obtained on Exposure of the Wool to a Germicidal Lamp or a Fluorescent Sunlamp for 24 Hours

Reagent (see facing page)	Solvent	Proportions by weight for 1 g. of wool: Reagent	Proportions by weight for 1 g. of wool: Solvent	Lamp	Protection, percent*
	Applied by evaporation impregnation				
I	Ethanol	0.71	56	Germ.	20
I	Water	0.71	71	Germ.	−10
II	Ethanol	0.17	23	Germ.	30
II	Ethanol	0.17	23	Sun	45
III	Ethanol	0.17	23	Sun	50
III	Ethanol	0.17	23	Germ.	40
	Applied by dyebath procedure, 1 hr. at 90°–100°, unless stated otherwise.				
II	0.25% aq. H_2SO_4	0.5	50	Germ.	80
II	2.0% aq. H_2SO_4	0.13	19	Germ.	65
II	2.0% aq. H_2SO_4	0.13	19	Sun	90
IV	2.0% aq. H_2SO_4	0.13	19	Sun	60
—	2.0% aq. H_2SO_4	—	19	Sun	−10
—	5.8% aq. maleic acid	—	24	Germ.	40
IV	2.0% aq. maleic acid	0.071	36	Germ.	60
IV	2.0% aq. maleic acid	0.071	36	Sun	100
V	2.0% aq. maleic acid	0.071	36	Sun	85
V	2.0% aq. malonic acid	0.071	36	Sun	90
V	2.0% aq. fumaric acid	0.071	36	Sun	100
V	2.0% aq. sulfamic acid	0.071	36	Sun	100
V	Acetic anhydride	0.071	39	Sun	−35
V	0.36% aq. H_2SO_4	0.071	36	Sun	100
V	50% aq. acetic acid	0.071	36	Sun	75
V	0.1 *N* buffer, pH 1.41	0.071	36	Sun	100
V	0.1 *N* buffer, pH 1.88	0.071	36	Sun	100
V	0.35% aq. H_2SO_4†	0.071	36	Sun	100
V	0.35% aq. H_2SO_4‡	0.071	36	Sun	−35
V	0.35% aq. H_2SO_4**	0.071	36	Sun	10
V	2.4% aq. H_2SO_4 + 7.1% $Na_2SO_4 \cdot 10H_2O$	0.071	11	Sun	90
V	2.4% aq. H_2SO_4 + 7.1% $Na_2SO_4 \cdot 10H_2O$††	0.071	11	Sun	65
V	0.36% aq. H_2SO_4	0.009	36	Sun	45
V	0.36% aq. H_2SO_4 + 0.04% histidine	0.018	36	Sun	65
V	0.36% aq. H_2SO_4 + 0.034% lysine hydrochloride	0.018	36	Sun	80
V	0.36% aq. H_2SO_4 + 0.038% arginine hydrochloride	0.071	36	Sun	55
V	2.8% wool hydrolysate, pH 1.37	0.18	36	Sun	70
—	5.9% aq. epichlorohydrin	—	36	Sun	0
V	0.36% aq. H_2SO_4‡‡	0.071	36	Sun	100
V	3.7% aq. HCl	0.071	36	Sun	100
—	2.5% aq. pyruvic acid	—	36	Sun	−50
V	0.36% aq. H_2SO_4‡‡	0.071	36	Sun	80
	Applied by dyebath procedure to silk cloth				
V	0.36% aq. H_2SO_4	0.059	29	Sun	65

* The reflectances of the samples, before and after radiation, were converted to K/S values by reference to a table [7]. The increase in K/S value was obtained by subtracting the initial value from the final value. Percent yellowing was determined by multiplying by 100 the ratio of the increase in K/S value of the treated sample to that of the accompanying control. Percent protection was calculated by subtracting the percent yellowing from 100, i.e.,

$$\text{Percent protection} = 100 - \left[\frac{A - B}{C - D}\right] 100$$

where A = K/S value of the treated cloth after exposure
B = K/S value of the treated cloth before exposure
C = K/S value of the untreated cloth after exposure
D = K/S value of the untreated cloth before exposure

† Heated 20 min.

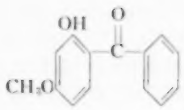
‡ After treatment with the absorber, the cloth was soaked in 1 *N* ammonium hydroxide for 60 min. at room temperature.

** After treatment with the absorber, the cloth was heated 1 hr. at 90° in 0.2 *M* buffer, pH 6.5.

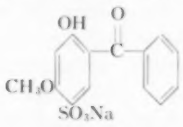
†† Washed in Accelerotor[3] with 0.1% sodium oleate at 40°–42° for 1 min. at 1500 r.p.m.

‡‡ Wool received the same pretreatment as given the preceding sample.

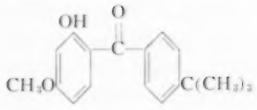
Ultraviolet light absorbing compounds listed in Table I



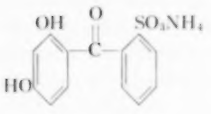
Compound I



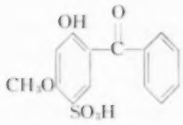
Compound II



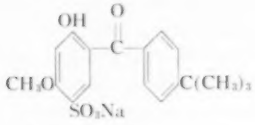
Compound III



Compound IV



Compound V



Compound VI

lamp yellowed the wool most rapidly. The fluorescent sunlamp, however, was preferred as a more natural form of radiation for accelerated yellowing; this lamp emits radiation corresponding to the shortest wavelengths present in sunlight but does not emit in the germicidal region. A discussion of the energy distribution of sunlight reaching the earth and that of common light sources was given by Gantz and Sumner [4]. The "black light" lamp was found to be relatively ineffective. The germicidal and fluorescent sunlamps were operated in a locked enclosure and provided with baffles to exclude extraneous light and protect personnel from the danger of exposure to these types of radiation.

In some experiments with the fluorescent sunlamp as the source of radiation and where the level of protection against yellowing was particularly high a minor bleaching was observed. This suggests that some portions of the spectrum bring about bleaching and yellowing of wool simultaneously, the latter predominating except when excellent protection against yellowing is obtained. In a limited number of experiments with roof-top sunlight, using a selected ultraviolet-transmitting polyethylene film to protect the wool from soiling, the information obtained was in general agreement with that obtained from lamp exposure experiments, with some mixed effects (bleaching) as discussed above.

Results and Discussion

The results obtained by the application of several of the more effective ultraviolet light absorbers under different conditions of treatment are reported in Table I. Application of water-insoluble, unsulfonated ultraviolet light absorbers from ethanol solution by means of evaporation impregnation resulted in a uniform deposition of the absorber over the surface of the cloth, with the probable introduction within the fiber of a minor portion of the substance; the protection thereby obtained varied from 20% to 50%. However, we were unable to produce a similar uniform deposition of the water-insoluble absorbers from aqueous suspensions. Thus, although water swells the fiber much more than alcohol, and would be expected to result in better introduction of the absorber within the fiber, this theoretical advantage is not obtained because of the insolubility of the absorbers in water. No protection was obtained from application under these conditions. However, the application of water-soluble benzophenone sulfonates having similar absorption spectra results in much better protection against yellowing. It seems probable that the effective ultraviolet light absorbers have certain chemical groupings properly arranged to combine (either by adsorption, chemical reaction, or some less clearly defined phenomenon) with certain reactive and sensitive sites in the wool protein. The aqueous medium swells and penetrates the wool fiber to a much greater extent than alcohol and enables the ultraviolet light absorber to penetrate the fiber to the reactive site. Evaporation impregnation tends to deposit more of the ultraviolet light absorber as a coating on the surface of the fiber and would give the best protection if the mechanism depended on a simple screening action.

Substances that gave essentially no protection against yellowing, when applied to wool by evaporation impregnation, are listed in Table II. The different solubility characteristics of the substances required the use of a variety of solvents; the water-soluble substances were applied from aqueous solu-

tion. Where more than one solvent was used, the results were similar. It is of interest to note that the Table includes substances known to absorb strongly in the ultraviolet but which nevertheless offer no protection against the yellowing of wool by ultraviolet light. This suggests that the protection obtained from ultraviolet light absorbers by the methods of application studied herein is not the result of a simple light screening action and that other factors are also involved. A similar result was recently reported by Knox, Guin, and Cockerell [8] in their study of the protective action of ultraviolet light absorbers against erythema. They state "While tannic acid, *p*-aminobenzoic acid, 2,4-dihydroxybenzophenone and 3-benzoyl-4-hydroxy-6-methoxy-benzenesulfonic acid were all effective ultraviolet light absorbers in 10% concentrations, *p*-amino-benzoic acid and 3-benzoyl-4-hydroxy-6-methoxy-benzenesulfonic acid were the most effective in preventing erythema."

Spectrophotometric studies on the rate of uptake of the ultraviolet light absorbers by wool from aqueous solution were made with three absorbers that we found to be most effective. The absorption spectra of these substances were determined over the range 250–320 mμ, against water as a reference solvent, and assay curves were prepared for each of them by measuring the optical density at the position of maximum absorption (284 mμ for Compounds IV and V, and 285 mμ for Compound VI). Concentrations were so chosen that the concentration–optical density curve was a straight line, and assay measurements were made at suitable dilutions to lie within this range. For these experiments, a solution of the reagent was prepared by dissolving a vacuum-dried and weighed portion (approximately 225 mg.) of the reagent in 200 ml. water to which 0.32 g. sulfuric acid and 0.8 g. sodium sulfate decahydrate had been added. The optical density of the solution (diluted 1:100 was measured and 100 ml. were heated to 50° under a reflux condenser. Four to five grams of wool flannel were added, and heating was continued to boiling. The optical density of the treating liquor was measured after varying intervals of time. The results are reported in Figure 5. The uptake was remarkably rapid; for Compound VI, 85% of the substance had been taken up at the first boil, and no further uptake was found during 45 min. of boiling. The curves show that uptake of Com-

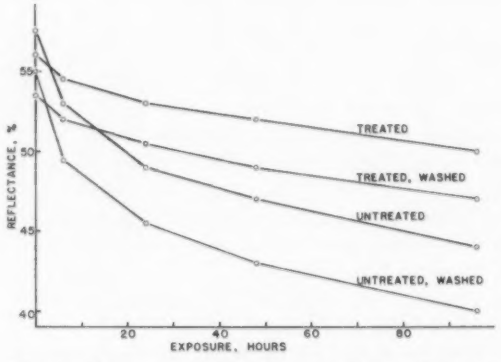


Fig. 1. Protection of wool flannel against yellowing by light, before and after washing with 0.1% sodium oleate at 1500 r.p.m. for 3 min. Cloth was treated with 2-hydroxy-4-methoxy-4′-*t*-butylbenzophenone-5-sodium sulfonate (Compound VI). Treated and untreated cloths were irradiated with a fluorescent sunlamp for the time indicated.

TABLE II. Substances That Gave Essentially No Protection against Yellowing by Ultraviolet Light When Applied to Wool by Evaporation Impregnation

Acetophenone
Anthracene
Anthraquinone-2-sodium sulfonate
Benzil
Benzoin
o-Benzoylbenzoic acid
Benzyl ether
4-*t*-Butyl phenyl salicylate
Camphor-2-sulfonic acid
5-Chloro-2-hydroxybenzophenone
Dibenzoylresorcinol
Dibenzyl
5,5′-Dichloro-2,2′-dihydroxydiphenylmethane
5,5′-Dichloro-2,2′-dihydroxydiphenylmethane sodium sulfonate (position undetermined)
Diphenyl
Diphenylacetic acid
Diphenyl disulfide
Diphenyl ether
Diphenylmethane
Diphenylmethane-4,4′-disodium sulfonate
Diphenylmethane-4-sodium sulfonate
Guaiacol sulfonic acid
Naphthalene
Phenyl benzoate
Phenyl salicylate
Phenyl sulfide
Phenyl sulfone
Phenyl sulfoxide
Tetrahydronaphthalene
p-Toluenesulfonic acid
Triphenyl carbinol
Triphenylmethane
Xanthpinnacol

pounds IV and V was much more complete when the treatment was terminated at room temperature rather than at the boiling point.

Studies of the protection against yellowing obtained by these treatments are reported in Figures 1–3, which also show the retention of this protection on washing with soap and warm water. The figures indicate that some protection was retained. As would be expected, the benzophenone sulfonates were not extracted by carbon tetrachloride after 30 changes of solvent in a Soxhlet extraction apparatus. The data in Table I marked with double dagger and double asterisk indicate that the wool was no longer protected after it was soaked in alkaline or slightly acid solutions. These results contrast with those reported in Figures 1–3, which give the extent of retention of the protection against yellowing after Accelerotor[3] [10] washing in 0.1% sodium oleate at 40°–42° and 1500 r.p.m. For these experiments, the treated wool flannel was that used for the rate of uptake experiments shown in Figure 5. Uptake of Compound VI was much more complete, at the boiling point, than that of the other two. This compound was also retained by the wool to a greater extent

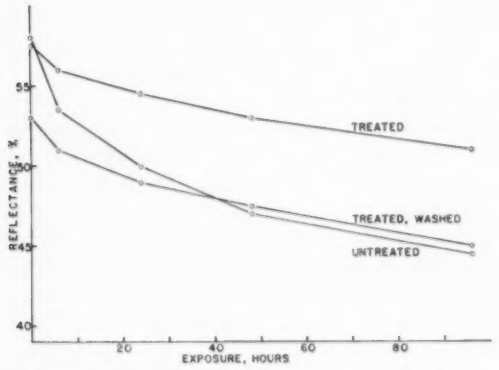


Fig. 2. Protection of wool flannel against yellowing by light, before and after treatment with 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (Compound V). The washing was with 0.1% sodium oleate at 1500 r.p.m. for 3 min. Treated and untreated cloths were irradiated with a fluorescent sunlamp for the time indicated.

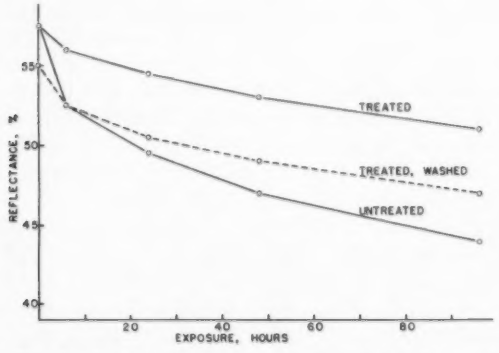


Fig. 3. Protection of wool flannel against yellowing by light, before and after treatment with 2,4-dihydroxybenzophenone-2′-ammonium sulfonate (Compound IV). The washing was with 0.1% sodium oleate at 1500 r.p.m. for 3 min. Treated and untreated cloths were irradiated with a fluorescent sunlamp for the time indicated.

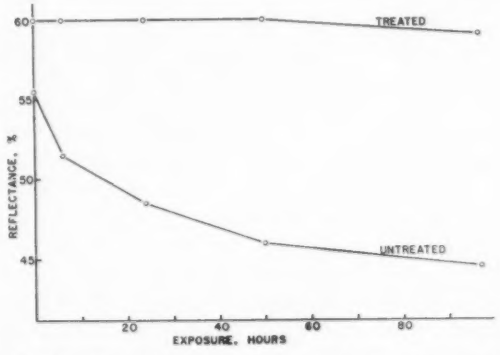


Fig. 4. Protection of wool flannel against yellowing by light, before and after treatment with 2,4-dihydroxybenzophenone-2′-ammonium sulfonate (Compound IV). Treated and untreated cloths were irradiated with a fluorescent sunlamp for the time indicated. An illustration of nearly complete protection.

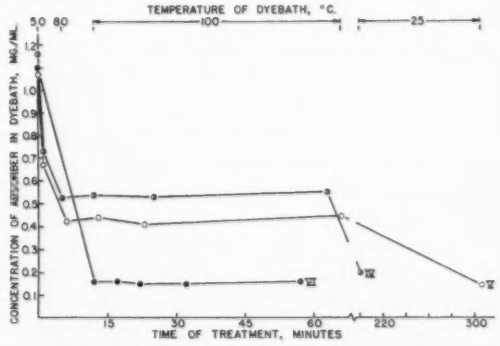


Fig. 5. Rate of uptake of substituted benzophenone sulfonic acids by wool flannel, as shown by exhaustion from the treating solution. The compounds are 2,4-dihydroxybenzophenone-2′-ammonium sulfonate (IV), 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (V), and 2-hydroxy-4-methoxy-4′-*t*-butylbenzophenone-5-sodium sulfonate (VI). The cloths treated were used for the experiments reported in Figures 1–3.

than the other two in the Accelerotor washing experiments.

Difficulties were sometimes encountered in the evaluation of the extent of yellowing ascribed to the exposure to the light source. Some substances yellow the wool during application, either due to the conditions of application or because the substances themselves are yellow. From a practical standpoint, it is difficult to evaluate the advantage gained by the application of a substance that results in a yellowing of the wool during application, but protects it from further yellowing on irradiation so that after irradiation both the treated and untreated wool cloths have about the same appearance and reflectance. Again from a practical standpoint, protection during the early stages of yellowing is of the most significance, since extreme yellowing by light seldom occurs during the life of the article. Under certain conditions of application, notably in the pH range of 1.3 to 1.7, a slight bleaching may accompany the application of the ultraviolet absorber; in this case the irradiated wool may have the same appearance and reflectance as the untreated wool, but may have been yellowed slightly during the exposure to the light. A third situation was also encountered, i.e., a slight bleaching during the exposure of the treated wool to ultraviolet light. These considerations lose their significance in the case of wool that has been yellowed extensively.

The substituted benzophenone light absorbers used in this study all have phenolic hydroxyls in the position *ortho* to the carbonyl group; the salts of these phenols are yellow. The variations in the response to washing, as reported in Figures 1–3, are probably related to the formation of yellow phenolic salts of the ultraviolet absorbers and to the degree of retention of the absorbers on the wool. It will be noted that treatment of cloth with Compound VI caused a slight yellowing, whereas the reflectance of cloth treated with Compounds IV and V was unchanged by the treatment. However, washing the treated and control cloths in the Accelerotor with 0.1% sodium oleate at 40°–42° and 1500 r.p.m. resulted in the control and cloths treated with Compounds IV and VI undergoing slight but significant loss of reflectance; cloth treated with Compound V was yellowed about twice as much as the others by the Accelerotor washing. Of the substances examined in this investigation, Compound IV is regarded as offering the best protection against light yellowing, based on the considerations discussed, i.e., no yellowing from the application of the substance to the cloth, a high degree of protection during the early stages of yellowing, and a minimum of yellowing from washing with soap. The lowered reflectance and increased rate of yellowing of untreated wool after washing in the Accelerotor is probably due to the uptake of alkali by the wool from the mildly alkaline environment.

A preliminary experiment suggested that the pH of the solution from which the sulfonated absorber is applied is an important factor in obtaining good protection. Several more experiments were therefore made with 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (V) in conjunction with several acids and buffers in the pH range 1 to 4. A 0.1 *M* HCl-KCl buffer was prepared and adjusted to pH 1.45. Addition of 0.1 g. Compound V to 50 ml. of this buffer lowered the pH to 1.41. The addition of 1.4 g. wool cloth, followed by heating at 90° for one hour, raised the pH to 1.55. As shown in Table I, there was no ultraviolet yellowing in 24 hr. exposure. Similar changes in the pH of the buffered ultraviolet light absorber solutions, during the treatment of wool, were observed repeatedly in the pH range 1.2 to 1.9; in each case there was no yellowing in 24 hr. exposure.

With various commercial samples of cloth, variations in protection were observed, possibly the result of some detail of processing. Figure 4 illustrates the high level of protection obtainable with a selected cloth and a period of exposure of 97 hr. The initial increase in reflectance over that of untreated cloth is ascribed to the acid, and not to the ultraviolet light absorber, in the solution used for treatment. This whitening was observed with a number of wools soaked in various acids in water or other solvents. The nearly complete protection is evidence of the ability of the treatment to preserve not only the normal reflectance of the wool but also that increase imparted by the treatment.

The results of experiments designed to elucidate the nature of the bond holding the ultraviolet light absorbers on the wool are not clearly defined. Data in Table I show that the best protection is obtained when the substance is applied from a strongly acid solution. In this respect, the uptake of the benzophenone sulfonates by the wool is similar to that of the sulfonic acid dyes. Data given in Table I show that competition for the ultraviolet light absorber

from basic amino acids or from wool hydrolysate added to the treating liquor did not decrease the protection obtained. This was true even when the amount of ultraviolet light absorber used was suboptimal. Experiments designed to block basic groups by prior reaction of the wool with either epichlorohydrin or pyruvic acid gave little or no impairment of protection. It is of interest to note that silk was also protected from ultraviolet yellowing by the same treatment that protects wool. Giles, Hassan, and Subramanian [5] studied the absorption of sulfonated azo dyes from aqueous solution by chitin. They found that the affinity of the chitin for the dye increased markedly with the increase in the number of benzene groups, i.e., with the increase in the planar area of the anion. They also found that the affinity decreases with an increase in the degree of sulfonation of the dye. These authors note that similar effects occur with wool. The observation that sulfonate groups, after the first, have a negative affinity is interpreted to mean that the planar groups and the sulfonate groups are adsorbed at specific sites and that the adsorbent does not possess cationic sites suitably located to bind the second sulfonate group of the anion. This second sulfonate group therefore remains in the water and tends to desorb the anion from the substrate. In view of these observations, it seems likely that the effectiveness of the ultraviolet light absorbers is dependent on the nature and relative positions of several of the groups in the sulfonated hydroxybenzophenones, as well as on the absorption spectrum of the substance.

Summary and Conclusions

Substituted benzophenones are effective in protecting wool against yellowing by ultraviolet light. The protection obtained is dependent on factors other than a simple absorption of ultraviolet light, since substances having similar absorption characteristics in the ultraviolet region vary greatly in the protection afforded by their application; also, the method of application of a given ultraviolet absorber has a strong influence on the amount of protection against yellowing obtained therefrom. Under the conditions of our experiments, the maximum protection is obtained from water-soluble ultraviolet absorbers, e.g., sulfonates, using dyebath techniques. The effectiveness of the application is also dependent on the acidity of the dyebath. Nearly complete protection against the yellowing of wool by ultraviolet light was obtained by the application of 2,4-dihydroxybenzophenone-2′-amonium sulfonate from a hot aqueous solution having a pH of 1.3–1.7.

Acknowledgments

The authors are grateful to the following manufacturers for gifts of the substances indicated. American Cyanamid Company: 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxybenzophenone-5-sodium sulfonate, 2-hydroxy-4-methoxy-4′-*t*-butylbenzophenone, 2,4-dihydroxy-4′-*t*-butylbenzophenone, 2-hydroxy-4-methoxy-3′-methylsulfonylbenzophenone, 2,4-dihydroxy-2′-chlorobenzophenone, and 2-hydroxy-4-methoxy-4′-aminobenzophenone. General Aniline and Film Corporation: 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, 2,2′-dihydroxy-4,4′-dimethoxybenzophenone, and the sulfonate of the last-named substance. Dow Chemical Company: 5-chloro-2-hydroxybenzophenone, dibenzoyl resorcinol, salol, and *t*-butyl salol. Sindar Corporation: 5,5′-dichloro-2,2′-dihydroxydiphenylmethane.

Literature Cited

1. Blackshear, C. C., *Am. Chem. J.* **14**, 455–473 (1892).
2. Coleman, R. A. and Peacock, W. H., TEXTILE RESEARCH JOURNAL **28**, 784–791 (1958).
3. Doer, W. H., *Ber.* **5**, 795–797 (1872).
4. Gantz, G. M. and Sumner, W. G., TEXTILE RESEARCH JOURNAL **27**, 244–251 (1957).
5. Giles, C. H., Hassan, A. S. A., and Subramanian, R. V. R., *J. Soc. Dyers Colourists* **74**, 682–688 (1958).
6. Gomberg, M. and Bachmann, W. E., *J. Am. Chem. Soc.* **49**, 236–257 (1927).
7. Judd, D. B., "Color in Business, Science, and Industry," New York, John Wiley and Sons, Inc. (1952).
8. Knox, J. M., Guin, J., and Cockerell, E. G., *J. Invest. Dermatol.* **29**, 435–444 (1957).
9. Remsen, I. and Hays, C. W., *Am. Chem. J.* **9**, 372–379 (1887).
10. Steigler, H. W., Glidden, H. E., Mandikos, G. J., and Thompson, G. R., *Am. Dyestuff Reptr.* **45**, P685 (1956).
11. Wedekind, E. and Schlenk, D., *Ber.* **44**, 198–202 (1911).

Manuscript received August 16, 1960.

Some Properties of Continuous-Filament Yarn

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Introduction

In the published theoretical considerations concerning the properties of continuous-filament yarn two principal assumptions have been made.

1. The diameter of the fiber, when compared with the diameter of the yarn, can be estimated as very small and substituted by a differential.

2. All fibers lie along uniform helices which have the same axis and the same number of turns per unit length, and every helix has a constant radius.

As there are usually more than 20 fibers in a cross-section of yarn, the first assumption seems to be justified. Even in the case of a small number of fibers in a cross-section, the theoretical considerations can be estimated as an approximation. The second assumption is now often objected to; there are a number of studies [1, 4, 8, 9, 10, 12, 15] stating the migration of fibers through the body of the yarn. It seems therefore that it is necessary to put the second assumption in a new form:

2a. All fibers lie along helices which have the same axis and the same number of turns per unit length, but the radius of the helix can vary along the length of the helix axis.

The new form of the second assumption requires new mathematical formulae for establishing the relationship between the properties of the yarn as functions of the twist and position of the fiber in the yarn.

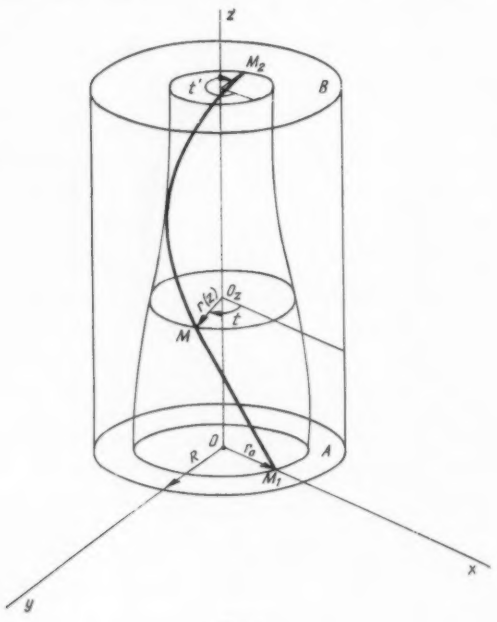

Fig. 1.

The Equation of the Fiber Position in the Yarn

Let us take the element of yarn AB (Figure 1) and the element of fiber M_1M_2 contained in it. It is useful to introduce the axes of Cartesian coordinates x, y, z, in such a way that axis z covers the axis of the yarn and axes x and y are perpendicular to the axis of the yarn. It is convenient to choose axis x passing through point M_1 of the fiber.

The radius of the fiber helix $OM = r$ will change along axis z, which can be denoted

$$OM = r(z) \tag{1}$$

The coordinates of every point of the helix will be given by the equations

$$\begin{aligned} x &= O_zM \cos t = r(z) \cos t \\ y &= O_zM \sin t = r(z) \sin t \\ z &= OO_z \end{aligned} \tag{2}$$

where t is the angle between the directions of radii of the helix in the cross-sections, which pass through points O and O_z of axis z.

In Equations 2, x and y are functions of z and t. But z also can be expressed as a function of t. Let h be the pitch of the helix. It is obvious, that $Oz = h$, when $t = 2\pi$. Therefore

$$z:h = t:2\pi \tag{3}$$

and

$$z = \frac{t}{2\pi} h \tag{4}$$

The introduction of Equation 4 into Equation 2 results in the coordinates becoming functions of parameter t:

$$\begin{aligned} x &= r'(t) \cos t \\ y &= r'(t) \sin t \\ z &= \frac{t}{2\pi} h \end{aligned} \tag{5}$$

Mathematical expression of the changes of $r'(t)$ can be obtained based upon the diagrams given by Morton [9]. For this purpose plane coordinates z, and $r(z)$ are chosen which represent the changes of radius of the fiber helix along the axis of the yarn.

The results of the investigations published by Morton [8] and Riding [12] show that the end points of the radius of the fiber helix form a line similar in shape to the line represented in Figure 2, which can be replaced by segments of a straight line, as it is shown in Figure 3. The changes of the radius in every segment are given by the equations:

between points O and z_1

$$r = r_0 + \frac{r_1 - r_0}{z_1 - z_0}(z - z_0) = r_0 + \frac{\Delta r_{0,1}}{\Delta z_{0,1}}(z - z_0) \tag{6a}$$

between points j and $j + 1$

$$r = r_j + \frac{\Delta r_{j,j+1}}{\Delta z_{j,j+1}}(z - z_j) \tag{6b}$$

In these equations, $\Delta r_{j,j+1}$ is the positive or negative difference of radii at the boundary points j and $j + 1$ of every segment of the length $z_{j+1} - z_j = \Delta z_{j,j+1}$ of the yarn.

Every cross-section of the continuous-filament yarn is approximately filled by the fibers to the same degree, therefore the numbers of the fibers migrating inside the yarn (for which $\Delta r_{j,j+1} < 0$) must equal the number of fibers which migrate to the outer zones ($\Delta r_{j,j+1} > 0$).

The value $\Delta r_{j,j+1}/\Delta z_{j,j+1}$ will change for every fiber along its length. If it is denoted by $1/b$, the equation for the first segment of the yarn (for the point z_0) will be

$$r = r_0 + \frac{1}{b_0}(z - z_0) \tag{7}$$

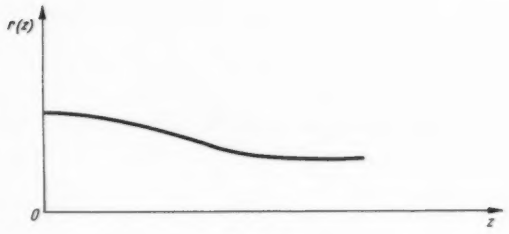

Fig. 2.

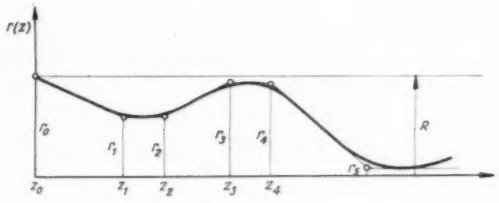

Fig. 3.

where r_0 can change its value from 0 (the fiber in the axis of the yarn) to R (the fiber on the surface of the yarn).

Substituting Equation 7 in Equations 2 or 5, we obtain

$$\begin{aligned} x &= \left(r_0 + \frac{t - t_0}{2\pi b_0} h\right) \cos t \\ y &= \left(r_0 + \frac{t - t_0}{2\pi b_0} h\right) \sin t \\ z &= \frac{t}{2\pi} h \end{aligned} \tag{8}$$

where $t_0 = \frac{2\pi}{h} z_0$—the value of parameter t for the initial cross-section.

Let us assume that for $t_0 = 0$ the fiber is passing through point 0 ($r_0 = 0$) and the slope of the line representing the ends of radii is constant along the segment of the yarn ($1/b$ = const.), the length of which equals h (the pitch of helix). Therefore

$(z - z_0) = h$, $t - t_0 = 2\pi$, and

$$r_1 = r_0 + (z - z_0)/b_0 = \frac{h}{b_0} \tag{9}$$

from which we obtain

$$b_0 = \frac{h}{r_1} \tag{9a}$$

Substituting Equation 9a into Equation 8 we obtain finally

$$x = \left(r_0 + r_1 \frac{t - t_0}{2\pi}\right) \cos t$$

$$y = \left(r_0 + r_1 \frac{t - t_0}{2\pi}\right) \sin t \qquad (10)$$

$$z = \frac{t}{2\pi} h$$

r_1 will be denoted as a periodical increase of the radius of helix.

In further consideration the differential of the length of the fiber will be necessary. It can be obtained from the formula:

$$dl = \frac{dl}{dt} dt = \sqrt{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}\, dt$$

$$= \sqrt{\left(r_0 + r_1 \frac{t - t_0}{2\pi}\right)^2 + \left(\frac{r_1}{2\pi}\right)^2 + \left(\frac{h}{2\pi}\right)^2}\, dt$$

$$= \frac{1}{2\pi} \sqrt{[2\pi r_0 + r_1(t - t_0)]^2 + r_1^2 + h^2}\, dt \qquad (11)$$

where $\dot{x}$, $\dot{y}$, $\dot{z}$ denote dx/dt, dy/dt and dz/dt, respectively.

If $t_0 = 0$, Equation 11 becomes

$$dl = \frac{1}{2\pi} \sqrt{(2\pi r_0 + r_1 t)^2 + r_1^2 + h^2}\, dt \qquad (12)$$

and if dl is calculated for the element of the yarn where $t = 0$

$$dl = \frac{1}{2\pi} \sqrt{(2\pi r_0)^2 + r_1^2 + h^2}\, dt \qquad (13)$$

Cross-Sectional Area of Fibers in an Elementary Ring of a Cross-Section of Yarn

In a cross-section of the yarn, the number of fibers having the same value of r_0 (distance from the axis of the yarn) is proportional to the area of the ring, the inner and outer radii of which are r_0 and $r_0 + dr_0$. The number of fibers passing through this ring will be calculated later on. Let us denote:

dn = number of fibers which are in the ring of radius r_0;
n = total number of fibers in a cross-section of yarn;
F_f = cross-sectional area of the fiber measured perpendicularly to its axis;
F_f' = cross-sectional area of the fiber measured perpendicularly to the axis of the yarn;
r_0 = radius of the ring;
β = angle between the direction of the axis of the yarn and the axis of the fiber which passes through the ring;
φ = cover factor of the cross-sectional area of the yarn by the cross-sectional area of the fibers;
F_y = cross-sectional area of the yarn.

The total cross-sectional area of fibers in the cross-section of the yarn is obviously nF_f', while the cross-sectional area of the yarn is F_y. It is very convenient to introduce a cover factor of the cross-sectional area of the yarn:

$$\varphi = \frac{nF_f'}{F_y} \qquad (14)$$

The cross-sectional area of the fibers which pass through the ring of radius r_0, measured perpendicularly to the axis of the yarn, is $F_f'dn$. On the other hand it equals the product of the area of the ring and of the cover factor. Therefore

$$F_f'dn = 2\pi r_0 dr_0 \varphi \qquad (15)$$

As

$$F_f = F_f' \cos\beta \qquad (16)$$

it is for the whole ring

$$F_f dn = F_f'dn \cos\beta = 2\pi r_0 dr_0 \cos\beta\varphi \qquad (17)$$

The value of $\cos\beta$ for $z = 0$ ($t = 0$) is given by the formula

$$\cos\beta = \frac{dz/dt}{dl/dt} = \frac{\dot{z}}{\sqrt{\dot{x}^2 + \dot{y}^2 + \dot{z}^2}} = \frac{h}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} \qquad (18)$$

where dl is the length of the element of helix, dz is the length of the element of the axis of the yarn.

Substituting Equation 18 into Equation 17 we obtain the cross-sectional area of fibers in the ring (measured perpendicularly to the fiber axis):

$$F_f dn = 2\pi r_0 dr_0 \varphi \frac{h}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} \qquad (19)$$

Hypotheses Concerning the Fiber Stresses in the Twisted Yarn

Although the technique of measurement is highly developed, the principal problem of whether or not the fibers in the twisted yarn are stressed is not definitely resolved.

All considerations concerning the structure of the yarn are based upon one of the two principles: (1) the fibers, when twisted into the yarn, change their slope, but no stresses or strains occur in them; or (2) the fibers, when twisted into the yarn, are strained proportionally to their distance from the yarn axis.

The migration of fibers rather supports the first principle, because it seems that even if there are some stresses in the outer fibers, their migration into the inner part of the yarn diminishes these stresses.

The diminution of the yarn diameter, when the twist becomes greater, suggests that there must be some stresses in the outer fibers which cause radial pressure. The known phenomenon of untwisting of yarns, when they hang freely, also supports the second principle.

The observations of Hearle and El-Behery [5] can support either principle, as it seems from the photographs shown in their letter that the outer fibers in the highly twisted yarn are similar to the fibers in the yarn with low twist but strained.

The difficulties with the assumptions suggest that it would be advantageous to study such phenomena as retraction of yarn, its strength, and elongation, first according to one principle and then according to the other and then to compare the results.

The Retraction of the Yarn

Hypothesis 1. As was mentioned previously, it is postulated in the first hypothesis that when the yarn is twisted the fibers change only their slope.

Retraction of the yarn is defined by the formula

$$s = l_1/l_0 \tag{20}$$

where l_1 is the length of the twisted yarn and l_0 is the length of the yarn in which fibers are parallel.

For very short segments of the yarn its length l_1 can be substituted by dz, the differential of its length, and l_0 must be substituted in this case by the mean length of segments of the fibers in the segment dz of the yarn

$$dl_0 = \frac{1}{n}\int dl\,dn \tag{21}$$

where dl is calculated from Formula 13.

Dividing the last formula by dz, we obtain

$$\frac{1}{s} = \frac{dl_0}{dz} = \frac{1}{n}\int \frac{dl}{dz}\,dn \tag{22}$$

The substitution of

$$dn = \frac{1}{F_f}\,2\pi r_0 dr_0 \varphi \frac{h}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} \tag{23}$$

from Equation 19 enables n to be computed as a function of the yarn parameter

$$n = \int dn = \int_0^R \frac{1}{F_f}\,2\pi r_0 dr_0 \varphi \frac{h}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}}$$

$$= \frac{\varphi h}{2\pi F_f}\left[\sqrt{(2\pi R)^2 + r_1^2 + h^2} - \sqrt{r_1^2 + h^2}\right] \tag{24}$$

where R is the radius of the cross-section of the yarn.

Substituting Equations 13 and 24 into Equation 22 we obtain

$$\frac{1}{s} = \frac{2\pi F_f}{\varphi h} \cdot \frac{1}{\sqrt{(2\pi R)^2 + r_1^2 + h^2} - \sqrt{r_1^2 + h^2}} \times \int_0^R \frac{\varphi}{F_f}\,2\pi r_0 dr_0 = \frac{2\pi^2 R^2}{h} \times \frac{1}{\sqrt{(2\pi R)^2 + r_1^2 + h^2} - \sqrt{r_1^2 + h^2}} \tag{25}$$

The retraction of the yarn is finally

$$s = \frac{h}{\pi R}\left[\sqrt{1 + \frac{r_1^2 + h^2}{(2\pi R)^2}} - \sqrt{\frac{r_1^2 + h^2}{(2\pi R)^2}}\right] \tag{26}$$

Introducing

$$2\pi R/h = 2\pi RT = g = tg\beta_R \tag{27}$$

where β_R is the angle between the fiber axis on the surface of the yarn and the direction of the yarn axis and T is the twist of yarn per unit length, we obtain

$$s = \frac{2}{g}\left[\sqrt{1 + \frac{1}{g^2} + \frac{1}{4\pi^2}\left(\frac{r_1}{R}\right)^2} - \sqrt{\frac{1}{g^2} + \frac{1}{4\pi^2}\left(\frac{r_1}{R}\right)^2}\right] \tag{28}$$

If the periodical increase of the radius of helix is small the terms containing r_1/R can be neglected and the formula for the retraction of the yarn will be

$$s = \frac{2\cos\beta_R}{1 + \cos\beta_R} \tag{29}$$

known as Braschler's formula [2].

Hypothesis 2. The considerations regarding the second hypothesis are based on the assumption that the length dz of the element of the twisted

yarn is created from the length dl_0 of bundle of parallel fibers. Hence

$$s = dz/dl_0 \tag{30}$$

The length of the fiber in the elementary segment of yarn, the length of which corresponds to the increase dt of parameter t, equals

$$dl = \frac{1}{2\pi}\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}\,dt \tag{31}$$

But the initial length of the fiber was dl_0. The strain of the fiber is therefore

$$\epsilon = \frac{dl - dl_0}{dl_0} = \frac{dl}{dl_0} - 1 \tag{32}$$

Substituting Equation 31 for dl and Equation 30 for dl_0, after simple transformations we obtain

$$\epsilon = \frac{s}{h}\sqrt{(2\pi r_0)^2 + r_1^2 + h^2} - 1 \tag{33}$$

If the values of ϵ are not great, we can assume the validity of Hooke's law. The stress in the fibers which pass through the ring of radius r_0 equals in this case

$$dW = E\epsilon 2\pi r_0 dr_0 \varphi \cos\beta \tag{34}$$

where E = Young's modulus.

The component parallel to the yarn axis equals

$$dP = dW\cos\beta = E\epsilon 2\pi r_0 dr_0 \varphi \cos\beta \tag{35}$$

Integrating the above formula for the whole cross-section of the yarn ($0 \leqslant r_0 \leqslant R$) we obtain

$$P = \int_0^R E\epsilon 2\pi r_0 dr_0 \varphi \cos^2\beta \tag{36}$$

Substituting Equation 33 for ϵ and Equation 18 for $\cos\beta$ we obtain

$$P = \int_0^R E\varphi\left[\frac{sh}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} - \frac{h^2}{(2\pi r_0)^2 + r_1^2 + h^2}\right] 2\pi r_0 dr_0 \tag{37}$$

from which we can compute the retraction of the yarn

$$s = \frac{\dfrac{4\pi P}{E\varphi} + \displaystyle\int_0^R \frac{h^2}{(2\pi r_0)^2 + r_1^2 + h^2}\,d(2\pi r_0)^2}{\displaystyle\int_0^R \frac{h}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}}\,d(2\pi r_0)^2}$$

$$= \frac{\dfrac{4\pi P}{E\varphi} + h^2\log\left(1 + \dfrac{2\pi R^2}{r_1^2 + h^2}\right)}{2h[\sqrt{(2\pi R)^2 + r_1^2 + h^2} - \sqrt{r_1^2 + h^2}]}$$

$$= \frac{\dfrac{P}{\pi R^2}\cdot\dfrac{g^2}{2\varphi E} + \frac{1}{2}\log\left(1 + \dfrac{g^2}{(r_1 T)^2 + 1}\right)}{\sqrt{g^2 + (r_1 T)^2 + 1} - \sqrt{(r_1 T)^2 + 1}} \tag{38}$$

If r_1 is small, the retraction of the yarn can be calculated from the simplified formula

$$s = \frac{\dfrac{P}{\pi R^2}\cdot\dfrac{g^2}{2\varphi E} + \log\dfrac{1}{\cos\beta_R}}{\dfrac{1}{\cos\beta_R} - 1} \tag{39}$$

which is similar to that in Budnikov's work [3].

It must, however, be remembered that the retraction is measured on the straightened yarn, i.e., on the yarn where the stress is very small. Therefore it can be assumed that $P = 0$, and then Formulae 38 and 39 become

$$s = \frac{\frac{1}{2}\log\left[1 + \dfrac{g^2}{\left(\dfrac{g}{2\pi}\cdot\dfrac{r_1}{R}\right)^2 + 1}\right]}{\sqrt{g^2 + \left(\dfrac{g}{2\pi}\cdot\dfrac{r_1}{R}\right)^2 + 1} - \sqrt{1 + \left(\dfrac{g}{2\pi}\cdot\dfrac{r_1}{R}\right)^2}} \tag{38a}$$

and

$$s = \frac{\log\dfrac{1}{\cos\beta_R}}{\dfrac{1}{\cos\beta_R} - 1} \tag{39a}$$

The retractions of the yarn for various values of r_1/R and g or β_R, computed from Formulae 26 and 38a, are given in Table I.

From Table I it is evident that the numerical values of retraction computed from different formulae are very similar. As the results of experiments published by Tattersall [14] were in rather full agreement with Formula 29, it seems that Formulae 26 and 38a are equivalent.

The Strength of the Yarn as a Function of the Twist

The considerations concerning the influence of twist of the yarn on its strength will be carried out in two steps: first some principal formulae will be developed, and then the strength of the yarn, according to the above mentioned hypotheses, will be computed.

If a tension P is applied to the yarn its element dz, being at the distance z from the initial point,

TABLE I. Retraction of Yarn Computed from Different Formulae

β_R	10°	15°	20°	25°	30°	35°	40°
$g = tg\beta_R$	0.1763	0.2679	0.3640	0.4663	0.5774	0.7002	0.8391
Formula 26							
$r_1/R = 1$	0.992	0.982	0.967	0.949	0.925	0.896	0.862
$r_1/R = \frac{1}{2}$	0.993	0.982	0.968	0.950	0.927	0.899	0.866
$r_1/R = \frac{1}{4}$	0.993	0.983	0.969	0.950	0.928	0.900	0.867
$r_1/R = 0$	0.993	0.983	0.969	0.951	0.928	0.901	0.868
Formula 38a							
$r_1/R = 1$	0.992	0.982	0.968	0.949	0.926	0.899	0.867
$r_1/R = \frac{1}{2}$	0.992	0.983	0.969	0.951	0.929	0.902	0.871
$r_1/R = \frac{1}{4}$	0.992	0.983	0.969	0.951	0.930	0.903	0.872
$r_1/R = 0$	0.993	0.983	0.969	0.952	0.930	0.904	0.873

will suffer some elongation a_z which will be proportional to the cross-sectional area of this element. Therefore the final length of the element dz will be

$$dz' = (1 + a_z)dz \tag{40}$$

Simultaneously the radius of the yarn will decrease and will be $r(z') = u_z r(z)$ (z' is the distance from the beginning of the element in the strained yarn). The coefficient of tightening u_z can be assumed as constant throughout the whole cross-sectional area of the yarn and equal to the ratio of the diameter of the strained yarn to the initial diameter of the yarn. Assuming this we obtain new coordinates of a point in a fiber

$$\begin{aligned} x' &= u_z\left(r_0 + r_1\frac{t - t_0}{2\pi}\right)\cos t \\ y' &= u_z\left(r_0 + r_1\frac{t - t_0}{2\pi}\right)\sin t \\ z' &= \int_0^z (1 + a_z)dz \end{aligned} \tag{41}$$

Substituting Equation 41 into Formula 13 we obtain

$$dl' = \frac{1}{2\pi}\sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + (1 + a_z)^2h^2}\,dt \tag{42}$$

The difference between the length of the element of the fiber in the strained yarn dl' and the initial length of the element of the fiber is the absolute elongation of the fiber. This value divided by the initial length of the fiber is its relative elongation

$$\epsilon = \frac{dl' - dl}{dl} = \frac{dl'}{dl} - 1 \tag{43}$$

which for a given ring is constant.

The relationship between the stress and strain for the fiber can be denoted as

$$Q = f(\epsilon) \tag{44}$$

The product of the cross-sectional area of fibers passing through the ring of radius r_0 in the yarn and of the stress in the fibers is the stress in the ring measured in the direction of the axes of the fibers

$$dW = Q2\pi r_0 dr_0 \varphi \cos\beta \tag{45}$$

(The stress is computed for the initial cross-sectional area of fibers.) The component in the direction of the axis of the strained yarn equals

$$dP = dW\cos\beta' \tag{46}$$

where β' is the angle between the fiber axis and the direction of the yarn axis.

It is obvious, that

$$\cos\beta' = \frac{dz'/dt}{dl'/dt} = \frac{(1+a_z)h}{\sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + (1+a_z)^2h^2}} \tag{47}$$

The whole force in the yarn equals

$$P = \int_0^R Q2\pi r_0 dr_0 \varphi \cos\beta\cos\beta' \tag{48}$$

and the relative stress computed for the initial cross-sectional area of fibers perpendicular to the yarn axis

$$Q_y = \frac{P}{\pi R^2\varphi} = \frac{1}{\pi R^2}\int_0^R Q2\pi r_0 dr_0 \cos\beta\cos\beta' \tag{49}$$

The function stress–strain is in general complicated. For our purposes, however, we can take according to Platt's conception [11] a simplified form

$$Q = A + B\epsilon \tag{50}$$

The last assumption facilitates the performance of further considerations according to both hypotheses.

Hypothesis 1. According to the first hypothesis it is assumed that, when the yarn is twisted, the fibers do not suffer any strain. Therefore in Formula 43, Equation 42 must be substituted for dl' and Equation 13 for dl. The elongation of the elementary segment of the fiber in such a case

$$\epsilon = \frac{\sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + (1 + a_z)^2 h^2}}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} - 1 \quad (51)$$

Substituting Equation 51 into 50 and then into 49 we obtain finally

$$Q_y = \frac{1}{\pi R^2} \int_0^R \left\{ A - B + B \frac{\sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + (1 + a_z)^2 h^2}}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} \right\} \times \frac{h}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} \cdot \frac{(1 + a_z)h}{\sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + (1 + a_z)^2 h^2}} 2\pi r_0 dr_0 \quad (52)$$

The integration of Equation 52 gives

$$Q_y = \frac{1}{g^2} \left\{ 2(A - B)k \log \frac{\sqrt{g^2 + (r_1 T)^2 + 1} + \sqrt{g^2 + (r_1 T)^2 + k^2}}{\sqrt{(r_1 T)^2 + 1} + \sqrt{(r_1 T)^2 + k^2}} + B u_z k \log \frac{g^2 + (r_1 T)^2 + 1}{(r_1 T)^2 + 1} \right\} \quad (53)$$

where $g = 2\pi RT$, $T = 1/h$, $k = (1 + a_z)/u_z$.

If $r_1 \sim 0$, i.e., if it is possible to assume that fibers lie on cylindrical surfaces, Formula 53 becomes

$$Q_y = \frac{1}{g^2} \left\{ 2(A - B)k \log \frac{\sqrt{g^2 + 1} + \sqrt{g^2 + k^2}}{1 + k} + B u_z k \log (g^2 + 1) \right\} \quad (54)$$

Hypothesis 2. When the second hypothesis is assumed, the elongation of the elementary segment of fiber is given by the formula

$$\epsilon = \frac{s dl'}{dz} - 1 \quad (55)$$

After substituting Equation 42 for dl' we obtain

$$\epsilon = \frac{s}{h} \sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + (1 + a_z)^2 h^2} - 1 \quad (56)$$

Substitution of Equation 56 into 50 and then into 49 gives

$$Q_y = \frac{1}{\pi R^2} \int_0^R \left\{ A - B + B \frac{s}{h} \sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + (1 + a_z)^2 h^2} \right\} \times \frac{h}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} \cdot \frac{(1 + a_z)h}{\sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + (1 + a_z)^2 h^2}} 2\pi r_0 dr_0 \quad (57)$$

Integrating this we obtain

$$Q_y = \frac{1}{g^2} \left\{ 2(A - B)k \log \frac{\sqrt{g^2 + (r_1 T)^2 + 1} + \sqrt{g^2 + (r_1 T)^2 + k^2}}{\sqrt{(r_1 T)^2 + 1} + \sqrt{(r_1 T)^2 + k^2}} + B u_z k \log \frac{g^2 + (r_1 T)^2 + 1}{(r_1 T)^2 + 1} \right\} \quad (58)$$

As it can be seen, Formulae 54 and 58 are identical although based on quite opposite assumptions.

For the analysis of the effect of every parameter on the strength of yarn it is convenient to represent Formula 54 or 58 in the form

$$Q_y = (A - B)C + B u_z D \quad (59)$$

where

$$C = \frac{2}{g^2} k \log \frac{\sqrt{g^2 + (q/2\pi)^2 g^2 + 1} + \sqrt{g^2 + (q/2\pi)^2 g^2 + k^2}}{\sqrt{(q/2\pi)^2 g^2 + 1} + \sqrt{(q/2\pi)^2 g^2 + k^2}}$$

$$D = \frac{1}{g^2} k \log \frac{g^2 + (q/2\pi)^2 g^2 + 1}{(q/2\pi)^2 g^2 + 1}$$

$$q = r_1/R$$

TABLE II. Values of C and D as the Functions of K, g, and q.

		g									
		0.2		0.4		0.6		0.8		1.0	
k	q	C	D	C	D	C	D	C	D	C	D
1	1	0.9795	0.9795	0.9241	0.9241	0.8475	0.8475	0.7636	0.7636	0.6807	0.6807
	0	0.9806	0.9806	0.9276	0.9276	0.8541	0.8541	0.7730	0.7730	0.6931	0.6931
1.2	1	0.9826	1.1754	0.9348	1.1089	0.8672	1.0170	0.7908	0.9163	0.7138	0.8168
	0	0.9831	1.1767	0.9378	1.1131	0.8731	1.0249	0.7996	0.9276	0.7253	0.8317
1.4	1	0.9843	1.3713	0.9415	1.2937	0.8800	1.1865	0.8094	1.0690	0.7372	0.9530
	0	0.9852	1.3728	0.9442	1.2986	0.8853	1.1957	0.8175	1.0822	0.7477	0.9703
1.6	1	0.9853	1.5672	0.9460	1.4786	0.8887	1.3560	0.8224	1.2218	0.7539	1.0891
	0	0.9862	1.5690	0.9485	1.4842	0.8937	1.3666	0.8300	1.2368	0.7639	1.1090
1.8	1	0.9864	1.7631	0.9491	1.6634	0.8951	1.5255	0.8318	1.3745	0.7663	1.2253
	0	0.9873	1.7651	0.9515	1.6697	0.8996	1.5374	0.8390	1.3914	0.7758	1.2476
2.0	1	0.9874	1.9590	0.9514	1.8482	0.8993	1.6950	0.8388	1.5272	0.7756	1.3614
	0	0.9881	1.9612	0.9536	1.8552	0.9039	1.7082	0.8457	1.5460	0.7848	1.3862

The values of coefficients C and D computed for various g and k are listed in Table II. The calcutions were carried out for $q = 1$ and $q = 0$.

As is seen from Table II the values of C and D are but little influenced by the change of q. The greater differences are seen when the value of k is increased.

The above observation suggests that the cylindrical structure of yarn can be used for calculations with adequate exactitude. On the other hand some attention must be paid to the factor k which includes influence of both elongation and tightening of the yarn on the yarn strength.

Breaking Elongation of the Yarn as a Function of the Twist

The change of the breaking elongation of the yarn as a function of the twist will be considered as previously according to the first and second hypotheses. The additional assumption made here is that the influence of the fiber torsion on its strength is negligible.

Hypothesis 1. According to the first hypothesis, from Equation 51 we have

$$(1 + \epsilon)^2[(2\pi r_0)^2 + r_1^2 + h^2] = u_z^2[(2\pi r_0)^2 + r_1^2] + (1 + a_z)^2 h^2 \quad (60)$$

Multiplying both sides by T we obtain

$$(1 + \epsilon)^2[(2\pi r_0 T)^2 + (r_1 T)^2 + 1] = u_z^2[(2\pi r_0 T)^2 + (r_1 T)^2] + (1 + a_z)^2 \quad (61)$$

The value of u_z is a function of the twist of the yarn and its elongation, but the influence of the changes of the elongation is rather small; therefore in the case of a yarn made of every kind of fiber it can be estimated as a function of the twist only. Therefore

$$a_z = \sqrt{(1 + \epsilon)^2[(2\pi r_0 T)^2 + (r_1 T)^2 + 1] - u_z^2[(2\pi r_0 T)^2 + (r_1 T)^2]} - 1 \quad (62)$$

With $r_0 = 0$ we obtain the least value of a_z, and this is the value of the breaking elongation of the weakest segment of the yarn. Formula 62 will then be

$$a_z = \sqrt{(1 + \epsilon)^2 + (r_1 T)^2[(1 + \epsilon)^2 - u_z^2]} - 1 \quad (63)$$

As it is known, u_z increases with the increasing twist of yarn. But on the other hand $(r_1 T)^2 \leqslant 0.025 g^2$, therefore it can be assumed that $(r_1 T)^2[(1 + \epsilon)^2 - u_z^2] \doteq 0$ and $a_z \doteq \epsilon$, as it was postulated by Platt [11] and partly by Hearle, El-Behery, and Thakur [6].

Hypothesis 2. According to the second hypothesis

$$\epsilon = \frac{s}{h}\sqrt{u_z^2[(2\pi r_0)^2 + r_1^2] + h^2(1 + a_z)^2} - 1 = s\sqrt{u_z^2[(2\pi r_0 T)^2 + (r_1 T)^2] + (1 + a_z)^2} - 1 \quad (64)$$

From this formula we obtain

$$a_z = \sqrt{\frac{(1+\epsilon)^2}{s^2} - u_z^2[(2\pi r_0 T)^2 + (r_1 T)^2]} \quad (65)$$

It is obvious that in this case if $r_0 = R$ the minimum value of a_z is obtained, and then

$$a_z = \sqrt{\frac{(1+\epsilon)^2}{s^2} - u_z^2[g^2 + (r_1 T)^2]} \quad (66)$$

or taking into account the previous observation that $(r_1 T)^2 \leqslant 0.025 g^2$ and can be neglected we obtain from Equation 66

$$a_z = \sqrt{\frac{(1+\epsilon)^2}{s^2} - u_z^2 g^2} \quad (67)$$

In this case the analysis of the changes in a_z is difficult as a_z depends on three functions of the twist s, u_z, and g. This analysis therefore must be carried out for every particular case. However we are able to make a statement valid for nearly all cases: the elongation received from this formula for various twists is not constant, as it was postulated by Kukin [7] and Żurek [16], and which seems to be in agreement with the experiments.

Influence of the Length of the Specimen on the Strength and Elongation of the Yarn

The previous considerations can be applied to the analysis of the effect of twist on the strength and elongation of very small segments of yarn. If broken segments are of length up to several hundred millimeters the reasoning must also include the effect of the changes in the fracture zone and variation of the fineness.

The length of the fracture zone can be obtained from the formula

$$l_z \doteq 0.7 \frac{\rho}{\mu} \quad (68)$$

where ρ is the radius of curvature of the fiber axis lying in the outer layer, μ is the coefficient of friction of the fibers.

With the increase of the twist the radius of curvature decreases and so does the length of the breaking area.

If we measure the strength and elongation of a bundle of parallel fibers whose length decreases, it is obvious that both the strength and elongation will increase.

So long as the length of specimen of yarn is smaller than the fracture zone its strength and elongation will be given by Formulae 54 or 58 and 65, in which A and B must be taken from the stress–strain diagram made for a bundle of parallel fibers.

When the length of a specimen of yarn is longer than the length of the fracture zone, then the calculation of strength and elongation of the yarn must be carried out stepwise. In the first step we calculate as before the strength, Q_{fz}, and elongation, a_{fz}, of a segment of the twisted yarn whose length is equal to the length of the fracture zone. Then we calculate the inner coefficient of variation of the yarn fineness $CV(x, y)$ where x is the length of the fracture zone and y is the length of the strained sample.

Then the strength of the yarn will be

$$Q_y = Q_{fz}[1 - Z \cdot CV(x, y)] \quad (69)$$

Z being a certain function of the relation of the sample length to the length of the fracture zone. This formula is similar to the formula published by Spencer-Smith [13].

The elongation of the yarn will be

$$a_y = \frac{a_{fz}}{a_0} \int_{F_1}^{F_2} f\left(\frac{P}{F}\right) \varphi(F) dF \quad (70)$$

where a_0 is the elongation of the bundle of parallel fibers whose length is equal to the length of the fracture zone,

$f\left(\frac{P}{F}\right)$ is a function illustrating the relationship between the elongation and the yarn stress $\left(\text{in this case } f\left(\frac{P}{F}\right) \doteq \frac{P - AF}{BF}\right)$,

$\varphi(F)dF$ is the probability of the area cross-section inside the strained segment of the yarn,

F_1 and F_2 are the least and the greatest cross-sectional areas of the specimen.

The above factors account for the appearance of maximum strength with a certain small twist ($g \doteq 0.2$) and also for some changes in the position of the maximum of the yarn elongation.

Conclusions

The theoretical considerations concerning the influence of the shape of the fiber axis in the twisted yarn show that: (a) The migration of fibers does not influence in any conspicuous manner such characteristics of the yarn as its retraction, strength, and elongation. Therefore the assumption of ideal shape of the helical path of the fiber axis can be used as a basis for theoretical calculations. (b) Two opposite assumptions of the changes in fibers, with twisted yarn, give very similar values of retraction of the yarn and the same value of the strength of the yarn. They show some differences only in respect of elongation. It seems, however, that the second assumption of strained fibers in the twisted yarn is more justified and should be used in theoretical considerations.

Appendix

The Change of Stress Along Fiber and Frictional Forces of the Fiber

When the formula of retraction of the yarn was developed, a tacit assumption was made that frictional forces acting on every element of the fiber are greater than the changes of stresses on both ends of the element of the fiber. Thanks to this it was assumed that the stress which arose in the element of the fiber when the yarn was twisted remained in it and could be changed only with relaxation. Let us denote

P = stress in the element of the fiber,
dl = length of the elementary segment of the fiber,
dP = value of the change of stress in the elementary segment of the fiber,
ρ = radius of the curvature of the elementary segment of the fiber, and
μ = coefficient of friction.

The normal pressure developed by the stress P equals P/ρ, and the frictional force acting on the unit length of the fiber equals $\mu P/\rho$.

If the stress is to remain unchanged in the fiber after the yarn is twisted, then

$$\frac{dP}{dl} \leqslant \mu \frac{P}{\rho} \tag{A1}$$

The simple transformation and division of both sides by dt gives

$$\frac{1}{P} \cdot \frac{dP}{dt} \leqslant \frac{\mu}{\rho} \cdot \frac{dl}{dt} \tag{A2}$$

According to the previous assumptions

$$P = EF_f\epsilon = EF_f \left[\frac{s}{h} \sqrt{(2\pi r_0)^2 + r_1^2 + h^2} - 1 \right] \tag{A3}$$

where E is Young's modulus, F_f is cross-sectional area of the fiber, and ϵ is elongation of the fiber from Formula 33. dP/dt can be calculated if instead of $\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}$ we use the equivalent Formula 12. Then

$$\frac{dP}{dt} = EF_f \frac{s}{h} \frac{(2\pi r_0 + r_1 t) r_1}{\sqrt{(2\pi r_0 + r_1 t)^2 + r_1^2 + h^2}} \tag{A4}$$

But for the considered cross-section of the yarn, $z = 0$ and $t = 0$, therefore

$$\frac{dP}{dt} = EF_f \frac{s}{h} \frac{2\pi r_0 r_1}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}} \tag{A5}$$

Substituting the above values into Equation A1 we obtain, after simple transformations

$$\frac{2\pi r_0 r_1}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2} - \frac{h}{s}} \leqslant \frac{\mu}{\rho} \left[(2\pi r_0)^2 + r_1^2 + h^2 \right] \tag{A6}$$

and finally

$$\mu \geqslant \frac{2\pi r_0 r_1}{\sqrt{(2\pi r_0)^2 + r_1^2 + h^2} - \frac{h}{s}} \cdot \frac{\rho}{(2\pi r_0)^2 + r_1^2 + h^2} \tag{A7}$$

The radius of curvature can be computed from the formula

$$\rho = \left[\frac{(\dot{M}^2)^3}{\dot{M}^2 \ddot{M}^2 - (\dot{M}\ddot{M})^2} \right]^{\frac{1}{2}}$$

where $\dot{M}^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2$, $\ddot{M} = \ddot{x}^2 + \ddot{y}^2 + \ddot{z}^2$, $\dot{M}\ddot{M} = \dot{x}\ddot{x} + \dot{y}\ddot{y} + \dot{z}\ddot{z}$, $\dot{x}$, $\dot{y}$, $\dot{z}$ denote dx/dt, dy/dt, dz/dt, respectively, and $\ddot{x}$, $\ddot{y}$, $\ddot{z}$ denote d^2x/dt^2, d^2y/dt^2, d^2z/dt^2.

Therefore the radius of curvature equals

$$\rho = \frac{[\sqrt{(2\pi r_0)^2 + r_1^2 + h^2}]^3}{\sqrt{[(2\pi r_0)^2 + r_1^2 + h^2][(2\pi r_0)^2 + 4r_1^2] - (2\pi r_0 r_1)^2}} \cdot \frac{1}{2\pi} \tag{A8}$$

Substituting this into Equation A7 we obtain

$$\mu \geqslant \frac{v^2}{\sqrt{1 + v^2 + w^2} - \frac{w}{s}\, 2\pi\sqrt{(1 + v^2 + w^2)(1 + 4v^2) - v^2}} \cdot \frac{\sqrt{1 + v^2 + w^2}}{} \tag{A9}$$

where $v = r_1/2\pi r_0$, and $w = h/2\pi r_0$.

Computations performed for various w with the constant value $r_1/r_0 = 1$ give minimum values of the coefficient of friction, as in the table below.

w	0.2	0.4	0.5	1.0
μ	0.497	0.249	0.202	0.112

It must be remembered that our considerations concerned the case when the frictional force was the result of the stress of the fiber, i.e., for the fiber lying in the outer zone of the yarn. For the parts of the fiber which are inside the body of the yarn the pressures are two and more times greater, and the value of μ must be reduced in the same proportion. It seems therefore that the assumption that the stress developed in every element of the fiber when the yarn is twisted, can remain (neglecting the relaxation) unchanged.

Literature Cited

1. Belicyn, N. M., *Tekstil' Prom.* **8**, No. 7, 22 (1948).
2. Braschler, E., "Die Festigkeit von Baumwollgespinnste," Zurich, 1935.
3. Budnikov, V. I., Budnikov, I. V., Zotikov, V. E., Kanarskij, N. J., and Pavlov, A. P., "Osnovy Prjadenija," Cast' II, Moscow and Leningrad, 1945.
4. Chaikin, M., Baird, K., Sutter, A. G., and Curtis, J., *Proc. Int. Wool Textile Res. Conf., Aust.* **E** 168 (1955).
5. Hearle, J. W. S. and El-Behery, H. M. A. E., TEXTILE RESEARCH JOURNAL **30**, 322 (1960).
6. Hearle, J. W. S., El-Behery, H. M. A. E., and Thakur, V. M., *J. Textile Inst.* **50**, T83 (1959).
7. Kukin, G. N., "Technologija shelka," Moscow and Leningrad, 1940.
8. Morton, W. E., TEXTILE RESEARCH JOURNAL **26** 325 (1956).
9. Morton, W. E. and Yen, K. C., *J. Textile Inst.* **43**, T463 (1952).
10. Pavlov, N. T. and Peisachov, V. K., *Tekstil' Prom.* **6**, No. 9–10, 17 (1946).
11. Platt, M. M., TEXTILE RESEARCH JOURNAL **20**, 1 (1950).
12. Riding, G., *J. Textile Inst.* **50**, T425 (1959).
13. Spencer-Smith, J. L., *J. Textile Inst.* **38**, P257 (1947).
14. Tattersall, G. H., *J. Textile Inst.* **49**, T295 (1958).
15. Włochowicz, A., *Przemysł Włókienniczy* **11**, 58 (1957).
16. Żurek, W., *Zeszyty Naukowe Politechniki Lódzkiej*, No. 14, 49 (1957).

Manuscript received August 25, 1960.

Variation in the Properties of Cotton Fibers with Length

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Abstract

Variation in the properties of fibers constituting a sample of cotton is one of their most remarkable characteristics. This variation has been studied, in the present paper, on 12 cottons, the fibers having first been sorted into groups based on quartile lengths. It is found that, in general, fiber strength, uniformity of strength, maturity, and reversals per unit length increase with increase in length group, while elongation per unit load decreases. The variation in fineness shows that the extreme length groups are finer than the middle ones. The significance of these findings for elucidating many problems of practical interest is indicated briefly.

Introduction

It is well known that fibers constituting a sample of cotton display great variation in their physical properties. Even in a pure strain, whatever the variety of cotton, the length of individual fibers may extend from ¼ in. to 2 in. or more in some cottons. The same is true of other fiber properties also, although the degree of variation will be different in each case. The problem has been investigated from various angles by several workers using different methods.

Thus Nanjundayya and Ahmad [13] in their studies on the variation of strength and weight per inch of cotton fibers found that the mean breaking load of whole fibers, fiber weight per unit length, and intrinsic fiber strength decrease with increase in fiber length. Iyengar [8, 9] observed a steady decrease in fiber weight with increase in fiber length, but he noted different trends in the variation of fiber maturity with respect to length. Rajaraman [14] studied the variation of fiber maturity with different length groups in some cottons and showed that the relationship between fiber maturity and length group in a cotton could be described in the form of a second degree curve. The increase in specific strength with increase in length when fibers are broken individually or in aggregates was observed by Grant and Morlier [5]. They also pointed out that the effective specimen length in bundle strength at "zero gauge length" actually lies between $\frac{1}{16}$ and $\frac{1}{32}$ in., and that the relation between specimen length and specific strength approximated a straight line when both the values are expressed as logarithms. In a later study on single fibers from American Upland cottons the above authors [11] concluded that the breaking load of single fibers, as well as elongation at break, increases with increase in fiber length, but weight fineness reaches a maximum for fibers near the modal length. In a recent work Rajaraman and Nanjundayya [15] came to the conclusion that as length group increases properties like individual fiber strength, Pressley strength index, and percentage of mature fibers progressively increase, while fiber weight per unit length decreases. Very recently Fiori et al. [3] in their studies on blending of cottons of widely varying maturity suggested that short fibers are finer and more immature than the long fibers. The relation between fineness and length was disputed by J. Shah [17], who produced data to show that the short fibers are coarser. But in their reply Sands et al. [16] pointed out that the discrepancy in the results of Shah might be due to the omission of fibers of less than 12/16 in. in his study. The above authors also supplied data on a number of *G. hirsutum* cottons to show that both the shortest and longest length groups have lower weight per unit length than the intermediate groups.

It will be noticed from the above review that many workers have apparently conflicting views, which may be due to differences in the methods of testing, properties studied, and the types of cottons exam-

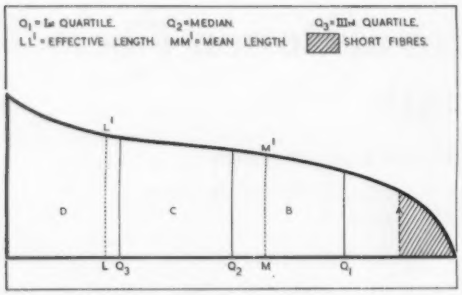

Fig. 1. Details of the grouping by length from the Baer Sorter.

ined. Earlier workers studied the properties of different length groups by sorting out the cotton into groups differing by $\frac{1}{8}$ or $\frac{1}{16}$ in. in mean length. As a particular length group, say $\frac{7}{8}$ in., may form the modal length of some short staple Indian varieties of cotton and may fall within the group of short fibers in a long staple cotton, the variation in other properties of such length groups does not convey much to the spinner. But if, instead of sectioning the staple in the above manner, it is divided into groups marked by statistical parameters such as upper quartile, median, and lower quartile, all cottons, whether of short or long staple, could be grouped together from a spinner's point of view, and similar trends, if any, among length groups could be studied. Such a study is likely to give additional information to spinners regarding the processing behavior of cottons.

Materials and Methods

Twelve cottons, comprising three cotton varieties from each of the four well-known botanical species of cultivated cottons, constituted the material for the study. From about a pound of lint of each cotton, ten representative slivers, each weighing about 1 g., were made. These slivers were drafted and doubled several times by hand so as to blend them thoroughly and parallelize the fibers in them. While one of these slivers was used for determining the length parameters of the cotton, the rest were sorted into the following four length groups, A, B, C, and D, with the help of a Baer Sorter as indicated in Figure 1.

A. Comprising fibers of lengths lower than the lower quartile (Q_1)
B. Comprising fibers of lengths lying between the lower quartile (Q_1) and median (Q_2)
C. Comprising fibers of lengths lying between the median (Q_2) and upper quartile (Q_3)
D. Comprising fibers of lengths longer than the upper quartile (Q_3)

It will be seen that group A consists essentially of short fibers (shown as shaded portion in Figure 1), which are responsible for the irregularity and weakness of yarns and for waste losses as a result of processes like carding, combing, etc. Group D consists of the longer fibers whose breakage during processing is an important factor to be contended with during the mechanical treatment of cotton. The other two length groups are important in as much as they constitute that half of the cotton in which are to be found the important length parameters which determine the details of the settings and speeds of the processing machinery.

Properties Studied

The fibers belonging to each of the four length groups were tested for mean length by the Baer Sorter. Fineness was determined gravimetrically and fiber maturity by the Caustic Soda Swelling Method [6]. Maturity coefficient was calculated adopting Iyengar's formula [10] $Mc = (M + 0.6H + 0.4I)/100$, where M, H, and I are the percentages of mature, half-mature, and immature fibers, respectively. Mature fiber weight was determined by dividing fiber weight by the maturity cofficient.

Specific surface area (in low position) was determined by employing the Arealometer [1, 12]. The breaking strength of flat bundles at zero (S_0) and $\frac{1}{8}$-in. (S_1) gauge lengths, the percent elongation at break (E), and the percent elongation per unit load (E/S_1), were determined on the Stelometer [2]. Structural reversals were counted by examining the fibers under a polarizing microscope [18] equipped with a $\frac{1}{4}$-wave red plate so as to produce elliptically polarized light.

Results and Discussion

The length particulars of the various cottons used in this investigation are given in Table I, and the results of the various fiber properties studied are presented in Tables II to VIII.

Fiber Weight per Unit Length

Statistical analysis of the data presented in Table III shows that the extreme length groups, A and D, have significantly lower fiber weight per unit length

TABLE I. Length Particulars of the Cottons

Cottons	Mean length, in.	Effective length, in.	Lower quartile, in.	Median, in.	Upper quartile, in.
G. barbadense					
1. Sea Island Andrews	1.33	1.60	1.20	1.42	1.56
2. S. K. M. Sudan	1.26	1.60	1.11	1.42	1.59
3. Karnak	1.10	1.40	0.86	1.16	1.37
G. hirsutum					
4. Acala 442	1.01	1.18	0.84	1.04	1.18
5. Arizona	0.99	1.23	0.78	1.06	1.22
6. MCU1	0.98	1.18	0.84	1.02	1.17
G. arboreum					
7. H 420	0.82	0.94	0.74	0.84	0.94
8. Gaorani 6	0.90	1.02	0.78	0.92	1.02
9. K5	0.87	1.03	0.79	0.91	1.03
G. herbaceum					
10. 1027 ALF	0.92	1.09	0.86	0.99	1.08
11. Kalyan	0.80	0.96	0.69	0.85	0.96
12. Westerns	0.82	0.94	0.72	0.85	0.94

TABLE II. Fiber Weight per Unit Length

Cottons		Full cotton	Length groups A	B	C	D
		micrograms/inch				
G. barbadense						
1. Sea Island Andrews		3.55	4.30	3.48	3.37	3.06
2. S. K. M. Sudan		3.46	3.83	3.65	3.31	3.04
3. Karnak		3.42	4.00	3.42	3.24	3.02
	Mean	3.48	4.04	3.52	3.31	3.04
G. hirsutum						
4. Acala 442		4.28	3.87	4.58	4.67	3.98
5. Arizona		3.98	3.62	4.51	3.97	3.81
6. MCU1		3.99	3.38	4.42	4.26	3.90
	Mean	4.03	3.62	4.50	4.30	3.90
G. arboreum						
7. H 420		5.11	4.61	5.05	5.70	5.07
8. Gaorani 6		4.53	4.04	4.90	4.96	4.23
9. K5		4.98	4.68	5.62	5.07	4.53
	Mean	4.87	4.44	5.19	5.24	4.61
G. herbaceum						
10. 1027 ALF		5.09	4.56	5.49	5.45	4.87
11. Kalyan		5.97	6.15	6.98	5.97	4.78
12. Westerns		4.74	4.50	5.24	4.86	4.35
	Mean	5.27	5.07	5.90	5.49	4.67
Grand mean		4.43	4.30	4.78	4.57	4.05

than the two middle groups, B and C. Further, groups D and B are the finest and coarsest, respectively. Taking the cottons individually, it is interesting to observe that in all the three *barbadense* cottons the fiber weight per unit length is highest for length group A, and gradually decreases, with the lowest value in length group D. In the remaining cottons the highest value occurs in length group B or in C, as in H 420 and Gaorani 6, and the lowest in length group A, except in the case of K5, Kalyan, and Westerns, where it lies in the length group D. The average results for *barbadense* cottons show a different trend from that shown by other cottons. The results on mature fiber weight presented in Figure 2 exhibit the same trend as those on ordinary fiber weight.

Fig. 2. Relationship between fiber weight and length group.

Maturity Coefficient

Maturity coefficient (Table III) increases with increase in length group in all cottons except Westerns, where the lowest value is shifted to group B. The average results show that the shortest length group A is significantly lower than the other three longer groups. When cottons are considered individually it is found that the differences between groups are significant in all cottons except Acala, Gaorani 6, 1027 ALF, and Western cottons.

TABLE III. Maturity Coefficient

Cottons		Full cotton	Length groups A	B	C	D
G. barbadense						
1. Sea Island Andrews		0.898	0.852	0.886	0.927	0.927
2. S. K. M. Sudan		0.928	0.901	0.919	0.941	0.950
3. Karnak		0.880	0.840	0.872	0.898	0.909
	Mean	0.902	0.864	0.892	0.922	0.929
G. hirsutum						
4. Acala 422		0.870	0.848	0.889	0.891	0.854
5. Arizona		0.908	0.873	0.913	0.925	0.924
6. MCU1		0.898	0.861	0.895	0.899	0.937
	Mean	0.892	0.861	0.899	0.905	0.905
G. arboreum						
7. H 420		0.941	0.917	0.943	0.944	0.959
8. Gaorani 6		0.902	0.886	0.907	0.914	0.906
9. K5		0.920	0.885	0.907	0.941	0.948
	Mean	0.921	0.896	0.919	0.933	0.938
G. herbaceum						
10. 1027 ALF		0.773	0.745	0.763	0.773	0.808
11. Kalyan		0.826	0.811	0.811	0.827	0.853
12. Westerns		0.892	0.895	0.881	0.892	0.899
	Mean	0.830	0.817	0.818	0.831	0.853
Grand mean		0.886	0.859	0.882	0.898	0.906

TABLE IV. Specific Surface Area Measured by Arealometer

Cottons		Full cotton	Length groups A	B	C	D
			mm.²/mm.³			
G. barbadense						
1. Sea Island Andrews		491	505	447	456	469
2. S. K. M. Sudan		480	492	470	454	464
3. Karnak		494	459	447	472	471
	Mean	488	483	455	461	468
G. hirsutum						
4. Acala 442		434	449	427	420	442
5. Arizona		444	436	423	425	429
6. MCU1		444	447	418	427	425
	Mean	441	444	423	424	432
G. arboreum						
7. H 420		341	359	344	342	349
8. Gaorani 6		379	405	377	367	371
9. K5		381	401	365	361	373
	Mean	367	388	362	357	364
G. herbaceum						
10. 1027 ALF		465	522	455	441	434
11. Kalyan		385	419	385	405	409
12. Westerns		385	398	383	390	398
	Mean	412	446	408	412	414
Grand mean		427	440	412	413	419

Specific Surface Area

From the results presented in Table IV it is evident that, in general, the specific surface area for group A is significantly greater than that of the other three groups. However, the same trend does not characterize all cottons. The lowest value is not restricted to any one length group, B or C being lower for *barbadense, hirsutum,* and *arboreum* cottons and B or D for *herbaceum* cottons.

Although the results obtained from specific surface area may appear contradictory to the earlier conclusions drawn from gravimetric fineness, this may be attributed to the dominant influence of immaturity on Arealometer specific surface area readings.

Fiber Strength

A general trend for breaking strength at zero and $\frac{1}{8}$-in. gauge lengths to increase with increase in length group will be noticed from Table V. The difference between extreme length groups is significant, thus establishing that the longer fibers are stronger than the shorter ones in all varieties of cottons studied in this investigation.

However, the increase in strength between successive groups does not follow a uniform pattern for strengths at zero and $\frac{1}{8}$-in. gauge lengths. A maximum increase of 8.3% is noticed between groups A and B in the case of strength at $\frac{1}{8}$-in. gauge length, while the over-all increase from A to D is 20.1%. For strength at zero gauge length, however, a maximum increase is observed between C and D, the value being 6.8%. The over-all increase between A and D is also lower for strength at zero gauge length, it being only 12.4%.

The fall in bundle strength from zero to $\frac{1}{8}$-in. gauge length is a measure of uniformity of strength. It will be noted from Table VI that the longer and finer cottons belonging to the *barbadense* species gave, on an average, a fall of about 35% while the short and coarse cottons of *herbaceum* species gave

about 50%. Mean fiber length and fineness are strongly correlated with uniformity of strength as will be seen from Figures 3 and 4, the correlation coefficients being -0.72 and $+0.92$, respectively. Further, the longer length groups are generally more uniform than the shorter ones. Individual samples which have similar strengths when measured at zero gauge length sometimes show large differences when measured at $\frac{1}{8}$-in. gauge length. For instance, variations in strength of length groups in H 420 and

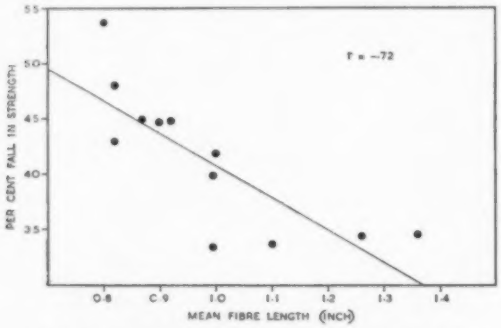

Fig. 3. Relationship between fiber length and uniformity of strength.

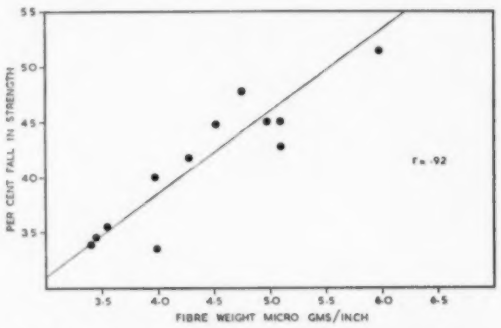

Fig. 4. Relationship between fineness and uniformity of strength.

TABLE V. Bundle Strength at Zero and $\frac{1}{8}$-in. Gauge Length

Cottons		Zero gauge length (S_0), g./grex					$\frac{1}{8}$-in. gauge length (S_1), g./grex				
		Full cotton	Length groups				Full cotton	Length groups			
			A	B	C	D		A	B	C	D
G. barbadense											
1. Sea Island Andrews		4.19	3.74	3.67	3.90	3.18	2.70	2.23	2.31	2.49	2.58
2. S. K. M. Sudan		4.74	3.51	4.12	4.64	4.81	3.10	2.61	2.97	3.08	3.09
3. Karnak		4.70	4.05	4.34	4.64	4.79	3.11	2.64	2.68	2.87	3.14
	Mean	4.54	3.77	4.04	4.33	4.59	2.97	2.49	2.65	2.82	2.94
G. hirsutum											
4. Acala 442		4.12	3.89	4.09	4.19	4.19	2.40	2.15	2.21	2.29	2.40
5. Arizona		4.06	3.76	4.03	3.97	4.10	2.44	2.05	2.08	2.19	2.38
6. MCU1		3.99	3.60	3.73	3.77	3.91	2.65	1.86	2.06	2.09	2.21
	Mean	4.06	3.75	3.95	3.98	4.07	2.50	2.02	2.12	2.19	2.33
G. arboreum											
7. H 420		3.93	3.57	3.45	3.56	3.72	2.25	1.88	2.06	2.25	2.44
8. Gaorani 6		4.35	3.66	3.96	3.94	4.25	2.40	2.14	2.34	2.45	2.52
9. K5		4.33	3.89	4.04	4.18	4.55	2.38	1.67	2.05	2.26	2.55
	Mean	4.20	3.71	3.82	3.89	4.17	2.34	1.90	2.14	2.32	2.50
G. herbaceum											
10. 1027 ALF		4.43	4.13	4.28	4.52	4.52	2.44	2.30	2.30	2.40	2.42
11. Kalyan		3.64	3.74	3.78	3.73	3.94	1.68	1.53	1.64	1.69	1.72
12. Westerns		4.14	4.12	3.99	4.12	4.20	2.16	1.87	2.18	2.21	2.32
	Mean	4.07	4.00	4.02	4.13	4.22	2.09	1.90	2.04	2.10	2.15
Grand mean		4.22	3.81	3.96	4.08	4.26	2.48	2.08	2.24	2.36	2.48

TABLE VI. Percent Fall in Strength from Zero to ⅛-in. Gauge Length

Cottons		Full cotton	Length groups A	B	C	D
G. barbadense						
1. Sea Island Andrews		35.6	42.5	37.1	36.2	38.3
2. S. K. M. Sudan		34.6	24.7	27.7	33.5	34.5
3. Karnak		33.8	34.8	38.2	37.0	32.5
	Mean	34.7	34.0	34.3	35.6	35.1
G. hirsutum						
1. Acala 442		41.8	44.6	46.1	45.6	42.5
2. Arizona		39.6	45.5	48.0	45.2	42.3
3. MCU1		33.6	48.2	44.8	44.4	43.6
	Mean	38.3	46.1	47.0	45.1	42.8
G. arboreum						
7. H 420		42.8	47.5	42.0	36.8	34.8
8. Gaorani 6		44.8	41.8	40.8	37.6	41.5
9. K5		45.0	57.0	49.5	46.2	44.0
	Mean	44.2	48.8	40.1	40.2	40.1
G. herbaceum						
20. 1027 ALF		44.9	44.3	46.0	46.9	46.7
11. Kalyan		53.8	58.6	56.8	55.0	56.2
12. Westerns		47.8	54.5	45.6	46.4	44.8
	Mean	48.8	52.5	49.5	49.4	49.2
Grand mean		41.51	45.3	43.6	42.6	41.8

Western cottons are not significant when tested at zero gauge length, but they become highly significant when tested at ⅛-in. gauge length.

The differences in tensile strength and uniformity of strength between different length groups are due to the presence of many weak links or structural heterogeneities along the length of the fibers. There may also be differences in the length and distribution of chain molecules, difference in spiral orientation, etc., in the different length grades of fibers constituting the sample. The higher strength and greater stiffness of the longer length groups suggest that the molecular chains in the longer fibers are more highly orientated than in the shorter ones.

Percent Elongation at Break

The differences in elongation between length groups (Table VII) are not found to be significant when all the cottons are considered together. However, there is a tendency for the elongation to increase with length group in *barbadense* and *hirsutum* varieties and to decrease in the *arboreum* variety; *herbaceums* do not show any particular trend.

Percent Elongation per Unit Load

Percent elongation per unit load (E/S_1) varies significantly among length groups in the cottons studied. A tendency is noticed for the longer length groups to be stiffer than the shorter ones. The values for length groups given in Table VII show that the elongation per unit load is maximum in group A in *barbadense, arboreum,* and *herbaceum* cottons, but in two *hirsutum* cottons the maximum is shifted to length group C. The lowest value occurs always in length group D in all cotton species.

Structural Reversals

Structural reversals are weak places in cotton where the fibers tend to break preferentially during tensile tests [18]. Reversals per unit length vary significantly among cottons and among length

groups. It is evident from Table VIII that the *barbadense* and *hirsutum* species contain appreciably higher numbers of reversals than the other two species. The longer length groups, in general, have a greater number of reversals. Since reversals are known to be weak places in a cotton, the association of a higher number of reversals with higher strength and uniformity of strength is at variance with the known fact; the higher number of reversals should weaken the fibers rather than strengthen them. Possibly the effect of reversals may have been masked by some other factors which influence bundle strength. However, when cottons within each species are considered, the stronger cottons generally have fewer reversals per unit length.

The findings reported herein reveal that differences among groups do not follow the same pattern in all cottons and that the fibers of different length groups differ significantly in their physical properties. Since mechanical treatments during processing act preferentially on certain length groups and since fibers act in bundles in yarn structure, the significance of these findings lies in their usefulness to the spinner. But before such use can be stressed it is necessary that the study be carried further and yarns spun from the sorted material to see how the spinnability improves with increase in length group.

Significance of Results

Although the results obtained from the present investigations are mainly of theoretical importance, they are not devoid of practical significance. Some of the practical aspects are briefly stated below.

Combing of Cottons

The results of this investigation give an approximate idea of what happens when a cotton is combed

TABLE VII. Percent Elongation at Break and Percent Elongation Per Unit Load

Cottons	Percent elongation at break (E)					Percent elongation per unit load (E/S_t)				
	Full cotton	Length groups				Full cotton	Length groups			
		A	B	C	D		A	B	C	D
G. barbadense										
1. Sea Island Andrews	6.33	6.2	5.7	6.1	6.4	2.34	2.79	2.49	2.43	2.47
2. S. K. M. Sudan	5.55	5.7	6.9	6.9	6.9	1.79	2.19	2.33	2.24	2.24
3. Karnak	6.00	5.8	6.2	6.4	6.5	1.93	2.20	2.30	2.22	2.07
Mean	5.96	5.90	6.20	6.50	6.60	2.02	2.39	2.37	2.30	2.26
G. hirsutum										
4. Acala 442	7.31	6.9	6.9	7.2	7.4	3.05	3.21	3.10	3.15	3.10
5. Arizona	5.40	5.3	5.6	6.2	5.8	2.21	2.58	2.69	2.84	2.42
6. MCU1	4.99	4.7	5.4	5.5	6.0	1.82	2.54	2.60	2.64	2.70
Mean	5.90	5.63	5.97	6.30	6.40	2.36	2.78	2.80	2.88	2.74
G. arboreum										
7. H 420	4.71	4.9	4.9	4.9	4.2	2.09	2.63	2.36	2.19	1.72
8. Gaorani 6	3.89	3.4	3.3	2.7	2.6	1.62	1.59	1.43	1.09	1.04
9. K5	4.91	5.6	5.3	5.4	5.7	2.06	3.34	2.58	2.41	2.25
Mean	4.50	4.63	4.50	4.33	4.17	1.92	2.52	2.12	1.90	1.67
G. herbaceum										
10. 1027 ALF	4.83	4.9	4.5	5.2	4.9	1.98	2.14	1.95	2.17	2.04
11. Kalyan	4.81	4.3	4.5	4.6	4.4	2.86	2.81	2.74	2.69	2.55
12. Westerns	4.16	4.6	4.6	4.6	4.4	1.92	1.74	2.11	2.06	1.90
Mean	4.60	4.60	4.53	4.80	4.57	2.25	2.23	2.27	2.31	2.16
Grand mean	5.24	5.19	5.31	5.47	5.43	2.14	2.48	2.39	2.34	2.26

TABLE VIII. Structural Reversals per Unit Length

Cottons	Full cotton	Length groups A	B	C	D
G. barbadense					
1. Sea Island Andrews	34	35	34	36	30
2. S. K. M. Sudan	22	18	24	23	21
3. Karnak	23	21	22	26	24
Mean	26	25	27	28	25
G. hirsutum					
4. Acala 442	25	24	26	25	26
5. Arizona	30	29	29	31	31
6. MCU1	30	28	30	32	32
Mean	28	27	28	29	30
G. arboreum					
7. H 420	20	18	19	20	22
8. Gaorani 6	16	16	15	17	16
9. K5	19	16	20	18	21
Mean	18	17	18	18	19
G. herbaceum					
10. 1027 ALF	16	16	14	17	16
11. Kalyan	10	9	11	10	9
12. Westerns	14	13	12	13	22
Mean	13	13	12	13	16
Grand mean		20	21	22	22

for better spinning performance. The removal of a relatively large percentage of short fibers, which have been shown to be weak and immature, is one of the reasons for the improved performance of the combed material in addition to the improvement in length and uniformity of length. Further, if combing could be as perfect as the sorting in the foregoing experiment, combing could lead to much more improved spinning performance that it does now.

Studies in Yarn and Fiber Structure

It is known [4, 7] that the presence of dissimilar fibers in a blend leads to a non-uniform distribution of these fibers throughout the yarn cross-section as a result of fiber migration effects. Since the fiber properties of cotton in different length groups vary significantly, it is evident that their behavior will be quite different from that of man-made staple fibers which are uniform in their fiber properties. This opens up new avenues of research into the arrangement of fibers in cotton yarn structure.

Summary

1. Physical properties of fibers from quartile length groups of 12 cottons, representing all the important cultivated species, have been determined.

2. The fiber weights per unit length of extreme length groups are generally lower than those of the middle groups, the longest length group being the finest.

3. Maturity coefficient increases with length group, indicating that within a cotton the longer fibers are generally more mature.

4. Mature fiber weight of the different groups shows a trend similar to that of gravimetric weight fineness.

5. Specific surface area (Arealometer) of the shortest length group is greater than those of the other three groups, which do not differ among themselves significantly.

6. Bundle strength (Stelometer) both at zero and at $\frac{1}{8}$-in. gauge length progressively increases with increase in length group.

7. The longer and finer cottons are generally more uniform in strength than the shorter and coarser varieties, and the longer groups within a cotton in general are more uniform in strength than the shorter groups.

8. Though no significant difference in elongation at break is observed among the length groups, the longer varieties generally have higher elongation than the shorter ones.

9. The longer length groups in a cotton are found to be stiffer than the shorter ones.

10. The longer length groups in general have a greater number of reversals, and within a species the stronger cottons generally have fewer reversals per unit length.

Acknowledgment

The authors wish to acknowledge the help rendered by the staff members of the Technology and Statistics Division of SITRA in carrying out the tests and analyzing the data collected. Their thanks are also due to the Director, SITRA, for permission to publish this work.

Literature Cited

1. American Society for Testing Materials, Committee D–13, ASTM Designation D1449–55T (1956). "Tentative General Methods of Testing Cotton Fibers."
2. American Society for Testing Materials, Committee D–13, *727* (1956).
3. Fiori, Louis A., Louis, Gain L., and Sands, Jack E., TEXTILE RESEARCH JOURNAL **29**, 706 (1959).
4. Ford, J. E., *J. Textile Inst.* **49**, T608 (1958).
5. Grant, J. N. and Morlier, O. W., TEXTILE RESEARCH JOURNAL **18**, 481 (1948).
6. Gulati, A. N. and Ahmad, N., *Indian Central Cotton Comm. Technol. Bull. Ser. B*, No. 20 (1935).
7. Hamilton, J. B., *J. Textile Inst.* **49**, T687 (1958).
8. Iyengar, R. L. N., *Indian J. Agr. Sci.* **9**, 305 (1939).
9. Iyengar, R. L. N., *Indian J. Agr. Sci.* **11**, 876 (1941).
10. Iyengar, R. L. N., *Indian Central Cotton Comm., Technol. Bull., Ser. B*, No. 40 (1949).
11. Morlier, O. W., Orr, R. S., and Grant, J. W., TEXTILE RESEARCH JOURNAL **21**, 6 (1951).
12. Morton, W. E. and Radhakrishnan, S., *J. Textile Inst.* **45**, T774 (1954).
13. Nanjundayya, C. and Ahmad, N., *J. Textile Inst.* **29**, T75 (1938).
14. Rajaraman, S., *Indian J. Agr. Sci.* **11**, 177 (1941).
15. Rajaraman, S. and Nanjundayya, C., *Indian Cotton Growing Rev.* **10**, 236 (1956).
16. Sands, J. E., Louis, G. L., and Tallant, J. D., TEXTILE RESEARCH JOURNAL **30**, 619 (1960).
17. Shah, J., TEXTILE RESEARCH JOURNAL **30**, 618 (1960).
18. Wakeham, H. and Spicer, N., TEXTILE RESEARCH JOURNAL **21**, 187 (1951).

Manuscript received September 7, 1960.

The Migration of Liquids in Textile Assemblies

Part IV: Penetration of Fabrics by Liquids

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Introduction

Penetration of a relatively small isolated mass of liquid through a fabric can be defined and measured in terms of the quantity of liquid transferred to a suitably selected underlying surface or substrate. Thus, if a drop of liquid is placed on the outside of a protective garment, the inside of which rests against the wearer's skin, penetration is said to occur if any of the liquid makes contact with the skin. If the inside of the garment rests against an absorbent substrate, such as a piece of blotting paper, the penetration can be measured quantitatively by comparing the amount of liquid collected in the blotting paper (after a stipulated time) with the amount originally placed on the outside of the fabric.

The rate and degree of penetration will depend primarily on the forces tending to move the liquid through the fabric, onto or into the receiving substrate. If the liquid droplet is placed gently on the outside of the fabric (or is already present in the fabric before penetration occurs) and penetration occurs solely because of capillary migration of the liquid we may define the effect as "capillary penetration" or "capillary transfer." If the liquid is placed gently on the outside, or is already present in the fabric, and penetration is promoted by applying an external mechanical force, we may define the effect as "expulsion penetration" or "pressure penetration." Expulsion penetration occurs, for example, when a weight is pressed on the top side of a wet spot in the fabric forcing the liquid into an underlying absorbent substrate. Centrifugal force can exert an expulsion effect. Gravity can also exert an expulsion effect. In the usual apparel fabrics, however, gravity has relatively little effect on droplets up to 20 mg., even when the liquid wicks poorly.

Both capillary and expulsion penetration can be called static penetrations because the liquid droplet's momentum before it enters the fabric is negligible or has a negligible effect. A third type of penetration may occur when the drop of liquid is thrown forcefully against the outside of the fabric. In this situation portions of the liquid may be carried through the fabric by momentum and the effect may be referred to as "impact penetration." Penetration of volatile liquids may also occur, under certain conditions, by an evaporation–condensation mechanism, an effect which is not considered in this discussion.

The present studies deal with the factors which influence all three types of penetration, capillary, pressure, and impact, through representative military apparel fabrics. Only relatively small isolated masses of liquid are considered, particularly droplets or splashes in the range of 0.1 to 30 mg. As in previous articles of this series [2] the liquids under consideration are substantially non-volatile so that any evaporation–condensation effect is negligible.

The experimental program consisted first in developing satisfactory methods for separating and measuring each of the three types of penetration. These methods were then used to study penetration quantitatively in a variety of liquid–fabric systems, attempting to relate penetration behavior to specific characteristics of both the liquid and the fabric.

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General Considerations

Transfer of Liquid to the Substrate

Since penetration is measured by the transfer of liquid from the fabric to an underlying substrate the mechanism of transfer and the factors that influence transfer require some consideration. It has been pointed out previously [3] that a mass of liquid in a non-uniform fibrous capillary system will tend to move into the narrower capillary spaces (provided the contact angle of the system is less than 90°). In a typical fabric the liquid will thus tend to move into the interior of the yarns and away from those regions where the individual fibers are widely spaced. In most apparel fabrics, particularly those designed for outerwear, the region of widest fiber spacing is the nap or fuzz on the fabric surface. When the fabric rests on a substrate the nap fibers tend to act as pillars or pedestals separating the denser portions of the yarns from the substrate. When fabric and substrate are pressed together the nap fibers tend to collapse, allowing the yarns to approach and contact the substrate. They also become compressed and approach one another closely enough to become an effective capillary system in themselves. These effects are shown in Figures 1–4. For transfer to take place at all it is necessary to have the substrate make contact with liquid that is part of the main continuous mass of liquid in the fabric. This can be done under the following circumstances: (a) if the nap is so sparse and weak that it does not effectively separate the liquid-laden yarns from substrate; (b) if sufficient pressure is applied to collapse the nap and allow the yarns to make contact; (c) if the pressure is sufficient to compress the nap to the point where it draws liquid out of the yarns by capillarity and brings the liquid down to the substrate; (d) if the nap fibers are crenulated and can act individually as liquid conduits. The quantity of liquid carried by this route is negligible compared with that carried in the channels formed by massed fibers. In all cases, of course, there must be enough liquid at the yarn surface to contact the adjacent substrate and form a liquid bridge.

Once the liquid is in contact with the substrate the rate of transfer and total quantity transferred will depend on how effectively the substrate can take liquid from the fabric. For any transfer to occur the substrate must be wettable. For rapid and extensive transfer the substrate should consist of a finer-pored system than the fabric and a system of at least as low a contact angle. It should also contact the liquid-bearing fabric above it over a relatively wide area, thus affording many individual channels of transfer. A fine-fiber, slightly sized or unsized paper such as the one used in these studies is quite satisfactory. It should be noted, however, that different papers or fabric substrates may give different absolute values for penetration.

Two-Layer Systems

The problem of substrates is closely related to the problem of penetration through two or more layers of fabric. In two-layer systems the underlayer acts first as a substrate for the top layer and secondly as a fabric transferring its liquid to the underlying true substrate. It is evident from the foregoing that the underlayer can have a profound effect on penetration. No data on two-layer systems are presented,

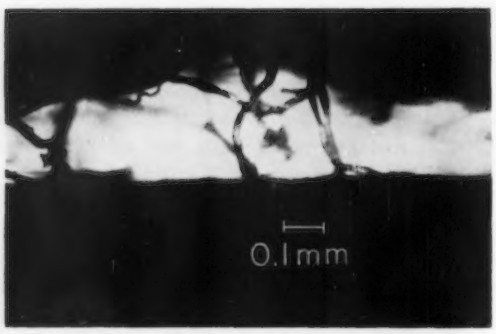

Fig. 1. Sateen lying on a cylindrical surface under a pressure of 0.04 lb./in.². Magnified 60 ×.

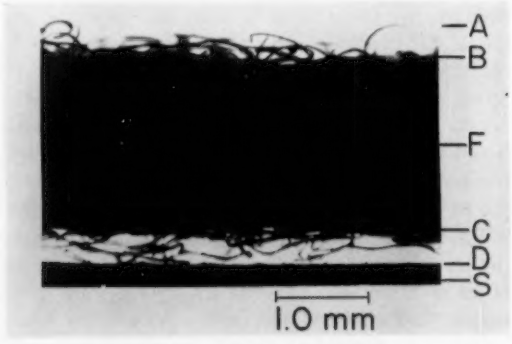

Fig. 2. Photomicrograph of jack shirting (F) lying on a substrate (S) under its own weight. Pressure = 0.0004 lb./in.² A-B and C-D represent upper and lower layers of nap, respectively. Magnified 40 ×.

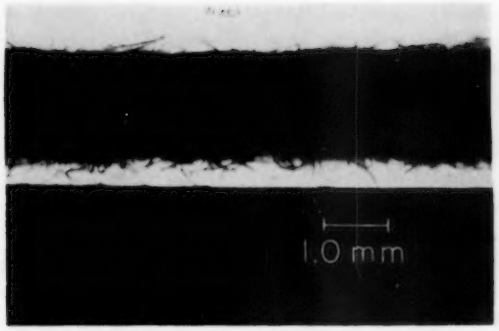

Fig. 3. Jack shirting lying under its own weight on a substrate surface. 0.0004 lb./in.^{2} pressure.

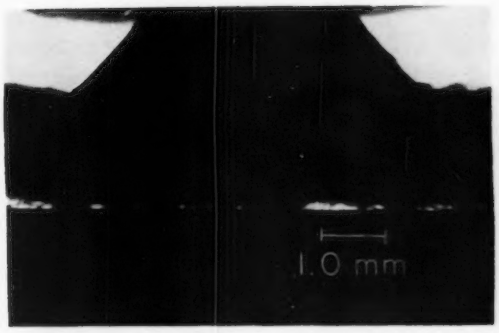

Fig. 4. Jack shirting under pressure on substrate surface. 0.076 lb./in.^{2} pressure.

since this study deals primarily with the more basic aspects of penetration.

Effect of Finishes

A few data are presented on penetration through water-repellent fabrics and oil-and-water-repellent fabrics. Since non-aqueous oily liquids were used the water-repellent fabrics showed no unusual behavior. The effect of oil-repellent and other functional finishes is not considered at any length, again because it is outside the present scope.

Reproducibility of Data

As in much other fabric work the replicability of data in penetration testing is variable. With the denser fabrics the test results in all three test methods described below were surprisingly duplicable. The more open and flatter fabrics tended to give larger deviations. In all cases a large number of replicate runs were made. The data presented below in tables represent in some cases the mean values of the replicates. In other cases, where so stated, they represent typical values selected from a series of runs.

Methods

Capillary Penetration: The Mandrel Test

The mandrel test takes its name from the smooth, hard, horizontally placed, cylindrical rod or mandrel upon which the test strip of fabric rests. The fabric strip is trimmed accurately to a known width and laid across the mandrel as shown schematically in Figure 5. A piece of smooth but absorbent paper, R, (mimeograph bond is quite satisfactory for most test liquids) is placed between the mandrel and the

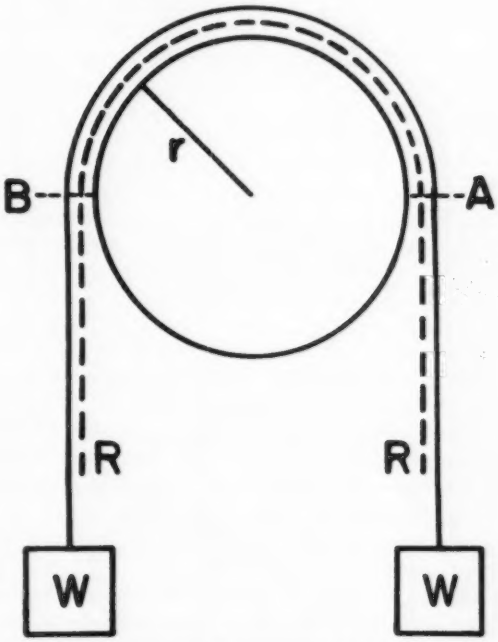

Fig. 5. Arrangement of components in the mandrel test. AB is horizontal plane through mandrel of radius r. W are weights attached to fabric strip. RR is paper substrate between mandrel and fabric strip.

fabric. Weights W are clipped to each end of the strip to provide any desired pressure against the mandrel. Assuming that the frictional force between fabric and mandrel (or paper and mandrel) is relatively negligible the pressure between fabric and mandrel over the arc A-B is given by the equation

$$P = \frac{W}{r \cdot d}$$

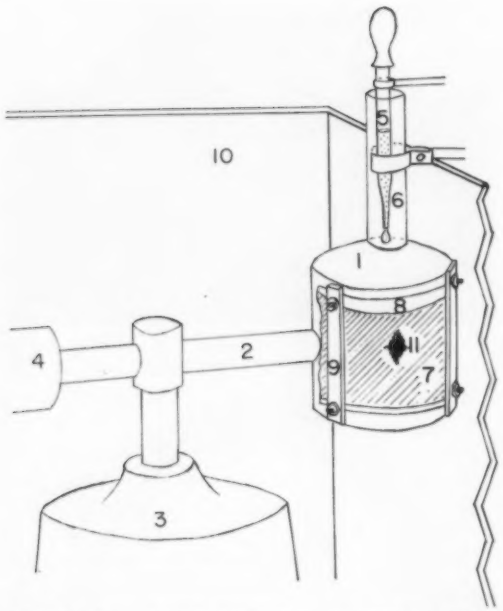

Fig. 6. Drop impact penetration apparatus. 1. Fabric holder. 2. Rotating arm. 3. Motor. 4. Counterweight. 5. Pipette. 6. Pipette shield. 7. Fabric. 8. Paper backing. 9. Fabric clamps. 10. Safety shield. 11. Drop mark ("hit").

where r is the radius of the mandrel, and d is the width of the fabric strip. If W is in grams and r and d in centimeters, P is expressed in g./cm^2. In most of the tests described below the mandrel was 3.8 cm. in diameter and the fabric strips were 1 in. wide. The weights, W, varied from about 10 g. to about 500 g. to provide the desired pressure.

In performing the test, a drop of liquid, D, of known weight is placed on the fabric. The fabric is left on the mandrel undisturbed for the desired length of time. It is then removed, and the underlying paper is examined for the presence of liquid that has penetrated.

The quantity of liquid penetrated was estimated by measuring the size of the spot in the paper. The test liquids were colored with a suitable dye, usually DuPont Oil Soluble Red, to facilitate measurement of the spot. The quantity required to color the liquid adequately is small. Two percent of the dye, based on the weight of the liquid, proved satisfactory in most instances. A comparison of the colored and uncolored liquids with respect to the way they wetted fabric, the size of drops formed from a dropper, and the contact angle against a single wool fiber, indicated that this addition did not substantially change the capillary properties of the liquids. This dye showed no tendency to be adsorbed from the liquids when tested on white woolen fabrics or paper.

The quantity of liquid that passed through the fabric into the paper in a given penetration test was estimated in the following manner from the area of paper that became colored. When a drop of colored liquid is placed on a sheet of mimeo paper, it soaks into the paper to form a colored spot. This colored spot expands rapidly at first, but less rapidly as time goes on. After a short time, the rate of expansion is quite slow, and after 24 hr., it is negligibly slow. The area of a spot produced by any given liquid measured after 24 hr. was found to be almost linearly proportional to the quantity of liquid applied, although the area of the spots produced as well as the rate of spreading varied to a certain extent with the liquid used. Because of this relationship "spot maps" can be prepared for any liquid, showing the size of the spots produced by various fixed quantities of liquid in the selected paper.

In preparing these spot maps for the test liquids being used, the ratio of the area of the colored spot to the quantity of liquid present was determined by using the smallest drops which could be conveniently produced. Several such drops were applied to the mimeo bond paper which was used in penetration experiments and the spots were measured after they had been allowed to expand for one day. Spot maps were used to estimate the quantity of liquid in the paper substrate after penetration had been allowed to proceed for a definite time interval. Due to the slight non-linearity of the weight–area relationship of these maps, the calculated weights tended to be low for large diameter spots and high for small diameter spots. The precision of this method, however, appeared to be fully adequate for the purposes of the present study and was remarkably good in view of the small quantities of liquid being measured.

A similar use of spot maps to estimate the quantity of liquid in aerosol droplets has recently been described [1].

Pressure Penetration: The Expulsion Test

A measured volume of the liquid to be tested (usually 1 drop weighing approximately 20 mg.) was applied to a swatch of the test fabric. The fabric was then allowed to lie undisturbed on a piece of mimeo paper (backed by a flat glass plate) for a

measured interval of time called the "wicking time." During this period the liquid had a chance to sink into the fabric and to start wicking. Little or no transfer occurred during the wicking period with most of the fabrics tested. At the end of the wicking time a weighted sheet of glass of known area was placed over the wet spot, and was allowed to remain for a measured interval of time, called the "expelling time." The fabric was then removed and the paper substrate was examined to see how much liquid, if any, was transferred. The quantity transferred was estimated by means of spot maps. In most of the tests conducted after the method had been proven in, an expelling pressure of 1 lb./in.^{2} was used. This was applied by using a 1-in. square of glass plate backed by a 1-lb. weight. The expelling time proved to be not particularly critical, and was usually taken as 1 min. The wicking time, on the other hand, usually had a strong influence on penetration. It was suitably varied but always carefully recorded.

Impact Penetration

The penetration that occurs when a fabric surface is struck by a drop of liquid moving toward it at high speed was studied by two methods. The first method, using relatively large drops, consisted in hitting the slowly falling drop with a rapidly moving swatch of fabric. In the second method, adapted to much smaller drops, the drop was thrown at the stationary fabric. In all cases the drop size and the speed of impact were controlled, and the quantity of liquid passing through the fabric was measured. In most instances, and unless otherwise noted, the relative speed of liquid drop and fabric at the time of contact was 40 miles per hour.

The apparatus used for producing collisions between drops and fabric in most of the experiments is shown in Figure 6. Essentially, it consists of a moving cylindrical fabric holder and a device for producing drops of liquid. The fabric sample was clamped on the fabric holder at the end of the rotating arm driven by the electric motor. Immediately beneath the fabric was placed the paper used for observing penetration by liquid. Before clamping the fabric and the penetration detector in place, a tension was applied to the fabric by a calibrated spring. The pressure between fabric and backing was, unless otherwise noted, adjusted to approximately 1 lb./in.^{2} With the fabric and its backing clamped in place, the assembly was rotated at a predetermined speed. When the apparatus was rotating at the desired speed, a drop of liquid was caused to fall through the path of the fabric in such a line that it was intercepted by the center portion of the fabric. In some cases, the drops were intercepted by either the upper or lower edge of the fabric sample. Hits of this kind were excluded from consideration.

At the moment of impact of the drop on the fabric surface, there was a splash, and a portion of the drop rebounded in small droplets. Some of the liquid that did not splash off was thrown off centrifugally. The remainder either stayed in the fabric or passed through the fabric.

In the early stages of the work it was considered of interest to find out what proportions of the impinging drops were splashed off, thrown off centrifugally, or retained by the fabric. The extent of splashing by different liquids and from different surfaces was investigated in the following manner. The liquids were colored with small amounts of dye. A band of paper was placed concentrically about the apparatus as shown in Figure 7. The droplets formed by the splash were caught by the paper upon which they formed a pattern of colored spots. The droplets thrown off centrifugally also formed a pattern of colored spots. The patterns were easily dis-

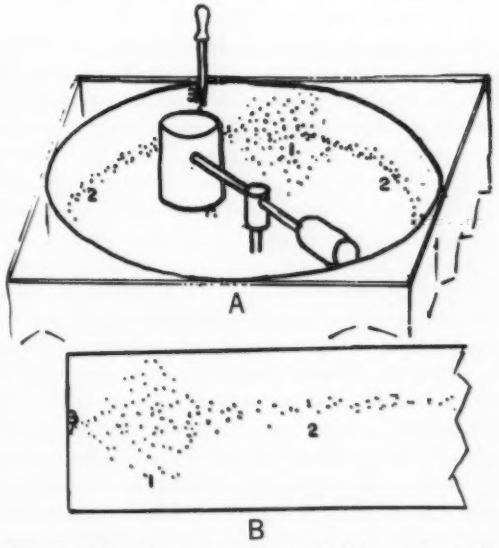

Fig. 7. Patterns produced from splashing and centrifugation. 1. Splash pattern. 2. Centrifugation pattern. 3. Position of fabric holder at time of impact. A. Paper cylinder in position. B. Paper cylinder unrolled.

tinguished from each other, thus allowing a quantitative estimate of the amount of liquid in each. As shown in the diagram, the splash pattern was roughly circular in shape, whereas the centrifugal pattern formed a narrow band. The splash patterns and the centrifugal patterns were studied quantitatively in order to find out what proportion of the impinging drop remained available for penetration.

The liquid thrown off by the centrifugal action described above came off in the form of very small droplets. These droplets were used for penetration experiments by placing fabric samples in their path. A convenient mounting site was provided by the wall of the safety shield. The centrifuged droplets presumably had an initial velocity of 40 miles per hour, the same as the speed of the rotating sample holder, and probably decelerated slightly during the 8 in. they traveled before striking the fabric. The pressure between the fabric samples and their paper backings was less than 0.05 lb./in.^{2}

Methods for Producing Drops and Determining Their Size

Three different drop producing methods were employed: the pipette method, the sieve method, and the centrifugation method. With these three methods, drops varying in size from 28 mg. down to 0.001 mg. (1 μgm.) could be produced.

In the pipette method, liquid is slowly forced from a medicine dropper-type pipette until a drop falls from its tip. The size of the drop is determined by the tip size of the pipette and the physical properties of the liquid. The average size of the drops delivered was determined by weight. With glass pipettes of various tip diameters, drops were obtained ranging from 3 to 40 mg.

A convenient way to make small drops is to drop a large drop through a sieve. The size of the sifted drops depends on the fineness of the sieve and can be estimated from the areas of the spots they form on paper. In order to obtain drops in different size ranges, 16-, 20-, and 40-mesh sieves were used. The size range of drops from a given sieve was quite reproducible and, in contrast to the pipette method, did not appear to depend on the nature of the liquid used. Drop sizes produced by this method ranged from 0.1 to 2 mg.

It was mentioned above that small droplets were thrown off the fabric holder by centrifugal effect and that these droplets could be used for penetration experiments. The bare brass sample holder was used to produce these drops because virtually all of the liquid that hit the brass was thrown off. The drop size in this method, as in the sieve method, did not vary much from liquid to liquid. With tri-*n*-butyl phosphate, the average size was 0.011 mg. (11 μgm.) per drop, and with Polyethylene Glycol 400, the value was 0.013 mg.

The method for measuring and detecting penetration was essentially identical to that used in the mandrel and expulsion tests. The liquids were colored with a suitable non-chromatographing dye (in most cases DuPont Oil Soluble Red). The penetrating portion of liquid was caught and retained by a piece of mimeo bond paper pressed closely between the holder and the back of the fabric. The quantity of liquid was estimated by comparing the spot size with a previously prepared spot map for the same liquid.

Materials

The numerous fabrics used in these studies are described below as they are introduced into the discussion. Most of the work was done with standard specification military or Navy fabrics such as the 14-oz. 85/15 wool-nylon jack shirting, 8.5-oz. cotton sateen, 9-oz. repellent finished sateen, 16-oz. wool melton, cotton twill, etc. A notable exception was the 5-oz. wool flannel, Botany style 404.

The liquids were selected to be substantially nonvolatile and inert toward the fabrics, but to vary in viscosity, surface tension, and contact angle against the various fibers.

Experimental and Results

Capillary Penetration

Among the various factors which influence capillary penetration, pressure of the fabric against the mandrel was one of the first to be studied. The penetration of jack shirting by 23-mg. drops of dibutyl butyl phosphonate was observed at pressures over the range 0.04–1.36 lb./in.^{2} Penetration generally occurred within a few seconds after placing the drop on the fabric, if it occurred at all during the 5-min. observation period employed in this experiment. No penetration occurred at pressures up to 0.62 lb./in.^{2} At pressures in the range 0.71–0.87 lb./in.^{2}, penetration occurred in some runs. At pressures of 0.94 lb./in.^{2} and above, penetration was observed in every run. Thus, with this liquid and fab-

TABLE I. Penetration of Sateen by 2.9-mg. Drops of Anilinoethanol over Various Periods of Time

Pressure of sateen against mandrel: 0.05 lb/in.²

Time*	5 min	1 hour	5 hours
No. of trials	16	15	16
No. of penetrations†	5	11	12
Ratio, penetrations to trials	0.31	0.73	0.75
Maximum quantity of liquid transmitted to paper in any trial	0.035 mg.	0.38 mg.	1.15 mg.
Average quantity of liquid transmitted to paper	0.0039 mg.	0.063 mg.	0.31 mg.
Average percent of drop transmitted to paper	0.13%	2.2%	11%

* The time shown is the length of time that elapsed between application of the drop and observation of the result.
† This line shows the number of trials in which the liquid passed through the fabric into the underlying paper.

ric there was a critical pressure above which the 23-mg. drop invariably penetrated the fabric. This result has been confirmed in a great number of experiments with other liquids and fabrics, and can be regarded as a general principle of the behavior of these systems. The critical pressure is characteristic of the fabric–liquid pair and also varies with the drop size. In a typical run using the same jack-shirting–dibutyl-butyl-phosphonate system, a fivefold increase in drop size was required for rapid penetration when the pressure was lowered from 1.27 to 0.04 lb./in.². Thus at constant pressure in a given fabric–liquid system, larger drops tended to penetrate to a greater extent than smaller drops, as might be expected. The penetration, however, did not increase regularly with drop size. Below a certain minimum critical size there was little or no penetration. In an intermediate size range the penetration did not vary greatly. When the dosage of liquid became large enough for gravity to be an important factor, the penetration increased very rapidly. Table I shows a typical set of data relating penetration to time. In many systems it was found that penetration took place in the first few minutes or not at all. Once a spot had formed in the underlying receiving paper, however, it tended to grow with time.

One of the most important factors influencing capillary penetration proved to be the weight of liquid per unit area of wetted fabric surface. This quantity, which we have called the *surface density*, is obtained by dividing the drop weight by the area of the wet spot formed on the fabric. The surface density of any spot is maximum at the instant the drop enters the fabric. The spot area increases with time, due to wicking, and the surface density correspondingly decreases. It was found in all cases, other factors remaining equal, that greater penetration occurred in spots of higher surface density. Liquids that wicked rapidly, and thus tended to attain a low surface density rapidly, also tended to penetrate less extensively. These liquids penetrated very soon after the drop was applied and the spot formed. In systems where wicking was slow and the surface density remained fairly high over a long time period the progressive penetration noted in Table I was obtained.

The mandrel test is usually performed by first stretching the fabric over the mandrel, then putting on the liquid. Thus, no time is allowed for wicking of the liquid in the fabric before the fabric is pressed against the mandrel surface. This test condition is referred to as zero wicking time. In a typical experiment with jack shirting, the usual procedure was reversed in order to observe the effect of allowing the liquid to wick for a measured time before placing the fabric on the mandrel. Details of the test conditions and the results observed are given in Table II. The quantity of liquid transmitted through the jack shirting diminished rapidly as the wicking time was increased. The difference between the penetration at zero wicking time and at a positive wicking time is very great, and is apparent with wicking times as short as 1 sec.

Penetration was found to be influenced by the physical properties of the penetrating liquid, insofar as they affected the wicking power. Liquids that wet the fabric but failed to wick laterally, thus maintaining a high surface density, tended to penetrate extensively, particularly over longer time periods. In some systems of this type, for example, PEG 400 or lactic acid on wool flannel, penetration of small drops occurred even at zero applied pressure.

The effect of fabric construction was, as might be expected, predominant in determining the rate and extent of penetration.

TABLE II. Effect of Wicking Time on Mandrel Penetration

Fabric: Jack shirting 65/20/15, wool/rayon/nylon
Liquid: Ucon 50HB55.
Pressure of fabric against substrate: 1 lb./in.²
Time allowed for penetration: 1 min.

Wt. liquid applied, mg.	Wicking time,* sec.	Quantity of liquid found in substrate paper, μgm.	
		Range	Average
40	0	1500–2000	1800
40	1	1–23	8
40	5	1–5	2
60	1	94–260	170
60	5	4–450	150
60	30	11–60	30
60	60	12–32	21
60	300	24–24	24

* "Wicking time" denotes the time elapsed between application of the liquid and placing of the fabric on the mandrel. Zero wicking time signifies that the fabric was placed on the mandrel before the liquid was applied. Where the wicking time is greater than zero, the liquid was applied to the fabric before it was hung on the mandrel.

TABLE III. Penetration of Fabrics in the Mandrel Test

Wicking time: zero
Penetration time: 5 min.
Pressure: 0.05 lb./in.²
Liquid and drop size: as shown below

Liquid	Drop size, mg.	Average percentage of liquid transmitted		
		Sateen*	Serge†	Jack shirting No. 9
Ucon-50-HB-55	10.8	1.2	0.005	None‡
Ucon-50-HB-55	14.4	1.5	0.01	None
Ucon-50-HB-55	20.0	2.3	0.42	None
Ucon-50-HB-55	32.4	4.8	—	None
Polyethylene Glycol 400	31	6.7	None	—

* 8½-oz. o.d. sateen.
† Air Force blue 100% wool 2 × 2 twill.
‡ Under these test conditions, a 100-mg. drop was required to penetrate the jack shirting.

Table III shows the resistance to penetration of three fabrics at 0.05 lb./in.² in the mandrel test. Although not widely different in cover, air permeability, or weight, these fabrics did differ widely in their resistance to penetration and illustrate the differences that may be expected. The most easily penetrated fabric, sateen, has a sparse nap of easily crushed cotton fibers. The serge also has a sparse nap, but its nap is composed of wool fibers, which are more difficult to crush than cotton fibers. The serge, it will be noted, was appreciably more resistant to penetration than the sateen. Jack shirting, the most resistant of the three fabrics, possesses an abundant nap of wool fibers. Its nap is not compressed very much by 0.05 lb./in.², and remains a barrier to capillary migration of liquid from the fabric to the underlying surface.

Pressure Penetration

It was found that the expulsion test is influenced by the following factors: (a) Type of fabric. (b) Type of liquid. (c) Drop size. (d) The time between applying the liquid and placing the weighted glass on the wet spot (the wicking time). The extent of wicking has an important effect on the penetration. (e) The weight and area of the weighted glass, i.e., the pressure applied. This pressure is called the expelling pressure. (f) The time that the weight is left on the wet spot. This time is called the expelling time. (g) The nature of the underlying surface that receives the liquid. Generally, fabrics showed high or low resistance to penetration corresponding to their behavior in the mandrel test. This was not always true. For example, a knitted fabric bearing a repellent finish was readily penetrated when expelling pressure was applied, even though it was not penetrated under mandrel test conditions. Nevertheless, the expulsion test resembles the mandrel test closely enough so that the importance of factors a, b, c, and g is obvious and requires no further discussion.

Wicking time is one of the more important variables governing penetration. Increasing the wicking time results in smaller transfer of liquid to the underlying surface. This result depends on the decrease in surface density of the liquid in the fabric.

As might be expected the degree of penetration is increased by increasing the expelling pressure, although the relationship is not linear. Considering the range of pressures between apparel fabrics and wearer's body, 1 lb./in.² represents a fairly heavy but realistic expelling pressure, and most of the expelling tests carried out during this work were made at 1 lb./in.² or less.

Lengthening the expelling time tended to increase the quantity of liquid transferred to the paper. In

general most of the transfer occurred immediately after applying the pressure, and the quantities transferred thereafter did not greatly increase the total quantity transferred. An exception to this was observed with very viscous liquids, which required an appreciable time in which to move from the fabric to the paper. After preliminary exploration an arbitrary expelling time of 1 min. was adopted as standard for most of the expulsion tests.

Of particular interest, in studying the mechanism of liquid transfer by expulsion, is the volume of interfiber space occupied by liquid and by air in the fabric before and after applying the pressure. To calculate the volume relationships the thickness of the fabric was measured at a very low pressure (actually 0.04–0.05 lb./in.^{2}, the lower limit of the compressometer range) and at 1 lb./in.^{2}, the expelling pressure used. Volumes of fiber and air under each square millimeter of fabric area were thus calculated. From the known weight of the liquid drop, the density, and the wicking area, the *average* volume of liquid under each square millimeter of fabric surface was also calculated. These quantities were then related to the amount of liquid expelled from the fabric to the substrate.

Three liquids were used: Ucon 50 HB 55, a Ucon thickened with a dissolved acrylic polymer, and a Ucon thinned with ethanol. The fabric was 8.5-oz. carded sateen.

The results are shown in Tables IV–VI. When the unmodified Ucon is used, significant expulsion (100 μgm. or more for each 20-mg. drop applied) occurs, even when 0.33 mm.^{3} of air is present under each mm.^{2} of wetted fabric. At 1 lb./in.^{2} there are 0.20 mm.^{3} of fiber and 0.12 mm.^{3} of liquid (average) within this same space. When the volumes of liquid and of air are approximately equal, a much larger quantity of liquid is expelled (600 μgm.). Even when enough liquid is present for 1600 μgm. to be expelled, there is still some air in the fabric. It should be emphasized that the calculated air space is based on the wicking area. Since the liquid is *not* uniformly distributed over the wicking area, there is much less air than average (and correspondingly more liquid than average) under the center of the spot. This is where penetration occurs.

Table V shows that the thickened Ucon does not come through the fabric until a somewhat higher proportion of air has been replaced by liquid. From this point of view, the thickened Ucon does not penetrate as well as the unmodified or thinned Ucon (Table VI). This effect, however, is more than counterbalanced at longer penetrating times by the slow wicking rate of the thickened Ucon. Similarly, the thinned Ucon is expelled even when the air space is quite large, but over a long penetrating period the high wicking rate will tend to decrease penetration. Thus the differences in ease of expulsion (due

TABLE IV. Volume Relationships in Expulsion

Ucon 50HB55. 20-mg. drop. 8½-oz. carded sateen. Thickness: 0.94* mm. at 0.05 lb./in.^{2}; .65* mm. at 1 lb./in.^{2} Weight of fiber under 1 mm.^{2} of fabric surface: 0.29 mg. Volume of fiber under 1 mm.^{2} of fabric surface: 0.20 mm.^{3}

Wicking time	Wicking area, mm.^{2}	Average vol. of liquid under 1 mm.^{2} of fabric surface,† mm.^{3}	Average vol. % of air under 1 mm.^{2} of fabric surface at 0.05 lb./in.^{2}‡	Average vol. % of air under 1 mm.^{2} of fabric surface at 1 lb./in.^{2}**	Quantity of liquid expelled (observed at 1 lb./in.^{2}), μgm.
1 sec.	50	0.40	36%	7.7%	1600
5 sec.	85	0.24	53%	32%	600
15 sec.	132	0.15	63%	46%	260
1 min.	170	0.12	66%	51%	100
5 min.	282	0.071	71%	58%	30
20 min.	350	0.057	72%	60%	12
60 min.	470	0.041	74%	63%	trace

* This numerical value is also equal to the total volume in mm.^{3} under 1 mm.^{2} of fabric surface.
† The quantity of liquid per mm.^{2} of fabric is higher near the center of the wet spot than near the edges of the wet spot.
‡ 21% of space is occupied by fiber.
** 31% of space is occupied by fiber.

presumably to viscosity) are less important from a practical point of view than the wicking rate.

Capillary vs. Pressure Penetration

The differences between capillary penetration and pressure penetration appear to be relatively small over a wide range of fabrics and liquids. Major differences occur, as might be expected, when the capillary properties tend to prevent wetting and entry of the liquid into the fabric. When a drop of liquid is placed on an air-permeable repellent fabric under mandrel test conditions, the liquid fails to enter the fabric regardless of the fabric–substrate pressure, and no penetration occurs. Under expulsion test conditions the drop is forced into the yarn and fiber interstices. Since it will not wick in the repellent material it is forced through to the substrate, and the penetration can thus be much greater than it would be with a similarly constructed non-repellent fabric. Typical comparisons of capillary and pressure penetrations are shown in Table VII.

TABLE V. Volume Relationships in Expulsion

Thickened Ucon 50HB55. Thickener: 1.6% of Polyco A-22 (polyacrylate) solids. 20-mg. drop. 8½-oz. carded sateen. Thickness: 0.94* mm. at 0.05 lb./in.²; 0.65* mm. at 1 lb./in.² Weight of fiber under 1 mm.² of fabric surface: 0.29 mg. Volume of fiber under 1 mm.² of fabric surface: 0.20 mm.³

Wicking time	Wicking area, mm.²	Average vol. of liquid under 1 mm.² of fabric surface,† mm.³	Average vol. % of air under 1 mm.² of fabric surface at 0.05 lb./in.²‡	Average vol. % of air under 1 mm.² of fabric surface at 1 lb./in.²**	Quantity of liquid expelled (observed at 1 lb./in.²), μgm.
1 sec.	38	0.53	22%	0%	1400
5 sec.	71	0.28	49%	26%	960
15 sec.	94	0.21	56%	37%	310
1 min.	113	0.18	60%	41%	55
5 min.	177	0.112	67%	52%	35
20 min.	263	0.076	70%	57%	Not determined
1 hr.	270	0.074	71%	58%	Trace

* This numerical value is also equal to the total volume in mm.³ under 1 mm.² of fabric surface.
† The quantity of liquid per mm.³ of fabric is higher near the center of the wet spot than near the edges of the wet spot.
‡ 21% of space occupied by fiber.
** 31% of space occupied by fiber.

TABLE VI. Volume Relationships in Expulsion

Thinned Ucon (50/50 mixture of Ucon 50HB55 and 95% ethyl alcohol). 15-mg. drop. 8½-oz. carded sateen. Thickness: 0.94* mm. at 0.05 lb./in.²; 0.65* mm. at 1 lb./in.² Weight of fiber under 1 mm.² of fabric surface: 0.29 mg. Volume of fiber under 1 mm.² of fabric surface: 0.20 mm.³

Wicking time	Wicking area,† mm.²	Average vol. of liquid under 1 mm.² of fabric surface,‡ mm.³	Average vol. % of air under 1 mm.² of fabric surface at 0.05 lb./in.²**	Average vol. % of air under 1 mm.² of fabric surface at 1 lb./in.²††	Quantity of liquid expelled (observed at 1 lb./in.²), μgm.
1 sec.	38	0.39	37%	9.2%	825
5 sec.	113	0.13	65%	49%	533
15 sec.	177	0.085	70%	57%	280
1 min.	177	0.085	70%	57%	37
5 min.	228	0.066	71%	59%	9

* This numerical value is also equal to the total volume in mm.³ under 1 mm.² of fabric surface.
† Error of measurement in the range of 100–200 mm.² is of the order of 10%.
‡ The quantity of liquid per mm.³ of fabric is higher near the center of the wet spot than near the edges of the wet spot.
** 21% of space occupied by fiber.
†† 31% of space occupied by fiber.

TABLE VII. Comparison of Mandrel and Expulsion Tests

Pressure: 1 lb./in.²
Expelling time: 1 min.
Liquid: Ucon 50-HB-55

Fabric	Wt. liquid applied, mg.	Wicking time, sec.	Weight penetration ratio = percent penetration = 100 × mg. penetrated/mg. applied	
			Mandrel test	Expulsion test
Jack shirting	60	10	7%	2.8%
Botany flannel	20	1	4.2%	5.2%
Botany flannel	20	5	4.5%	1.4%
Botany flannel	20	20	0.12%	less than 0.02%
Botany flannel	20	60	less than 0.02%	less than 0.02%
Knit underwear fabric, repellent finish	20	1	0%	30%
Knit underwear fabric, repellent finish	20	300	0%	19%

Impact Penetration

The first part of the experimental program on impact penetration was aimed at determining the relative importance of the various factors affecting this process. A series of inert and substantially non-volatile test liquids shown in Table VIII was used. These liquids differed with regard to surface tension, viscosity, and density.

Three fabrics were used: two military fabrics, sateen and jack shirting, and a non-military fabric, Botany 404 flannel. The sateen was 8.5-oz. cotton and carried no repellent finish. The jack shirting was 14-oz. 85/15 wool-nylon. Two other fabrics were studied briefly: a cotton duck and a special oxford treated with an oil-and-water-repellent finish.

Studies were made of the penetration of these fabrics by drops of various controlled sizes moving at 40 miles per hour relative to the fabric surface. The drops varied in size from 0.01 mg. (10 μgm.) to 28 mg. The weight percentage of impacted liquid which penetrated through the fabric was estimated. This is referred to as the "weight penetration ratio." It is calculated as 100 times the ratio of the weight of liquid carried into the absorbent paper behind the fabric to the weight of liquid hitting the fabric. The ratio of the number of hits (i.e., number of drops hitting the outside of the fabric) to the number of penetrations was also observed.

In the second part of the experimental program a single test liquid, diethyl sebacate, was used to determine the comparative penetration resistance of a series of fabrics and fabric combinations.

TABLE VIII. Impact Penetration of Fabrics by Liquids of Differing Viscosity

Average drop size: 20 mg.

Liquid	Viscosity, cp	Wt. penetration ratio = % penetration = 100 × mg. penetrated/mg. hit		
		Botany flannel	Jack shirting	8.5-oz. cotton sateen
Triethyl phosphate	1.3	—	—	3
Tri-*n*-butyl phosphate	1.8	—	—	1.4
Diethyl sebacate	5.4	6	0.5	0.5
Ethylene glycol	17	3.8	0.12	0.2
Diethylene glycol	30	3.8	0.0005	0.02
2-Anilinoethanol	54	0.2	—	0
Polyethylene Glycol 400	98	—	—	0

Several of these fabrics were also submitted to the mandrel test for static or capillary penetration.

The following relationships were evident from the data as shown in Tables VIII and IX:

1. Liquids of low viscosity penetrated to a greater extent than did liquids of high viscosity, i.e., they showed a higher weight penetration ratio. This is illustrated by the data in Table VIII. Diethyl sebacate, a liquid having a viscosity of 5.4 centipoises (at 25° C.) penetrated all three fabrics even at small drop sizes. Two liquids of high viscosity (2-anilino ethanol and Polyethylene Glycol 400) failed to penetrate the sateen.

2. Large drops penetrated the fabric more often than small drops, i.e., large drops showed a higher

TABLE IX. Effect of Drop Size and Fabric–Liquid System on Impact Penetration

Liquid	Av. size of drops hitting fabric, mg.	Ratio, number of penetrations to number of hits	Weight penetration ratio (%) = mg. penetrated × 100 ÷ mg. hit
	Botany 404 flannel		
Diethyl sebacate, viscosity = 5.4 cp	21	1	6
	1	0.8	16
	0.3	0.65	1
	0.1	0.28	2
	0.01	0.30	0.75
Ethylene glycol, viscosity = 17 cp	26	1	3.8
	1	1	6.5
	0.3	0.67	11
	0.1	0.37	6
	0.01	0.04	0.01
	8.5-oz. Cotton sateen (OD-7)		
Tri-*n*-butyl phosphate, viscosity = 1.8 cp	18.6	1	1.4
	3.7	1	0.54
	0.01	0.05	<0.05
Diethyl sebacate, viscosity = 5.4 cp	21	1	0.5
	1	0.4	0.04
	0.3	0.02	<0.001
	0.1	0.007	<0.001
Ethylene glycol, viscosity = 17 cp	26	1	0.2
	1	0.13	<0.001
	0.3	0.05	<0.001
	0.1	0.02	<0.001
	14-oz. Jack shirting 85/15 wool-nylon		
Diethyl sebacate, viscosity = 5.4 cp	21	1	0.5
	1	0.4	0.4
	0.3	0.03	0.01
	0.1	0.01	0.01
Ethylene glycol, viscosity = 17 cp	26	1	0.12
	1	0.3	1.7
	0.3	0.1	2.0
	0.1	0.05	0.2

ratio of penetrations to hits, but not necessarily a higher weight penetration ratio.

3. The weight penetration ratio varied not only with the viscosity of the test liquid, but also with the drop size and the type of fabric. The resistance of fabrics to penetration appeared to vary with the "cover" of the fabric; thus, the fabric showing the fewest holes when viewed against an illuminated background had the greatest resistance to impact penetration, i.e., it showed the lowest weight penetration ratio.

4. For each fabric–liquid pair there was an optimum drop size which gave the highest weight penetration ratio. For diethyl sebacate and sateen, this optimum drop size was 21 mg. For diethyl sebacate and Botany flannel, the optimum drop size was 1 mg. The smallest optimum drop size (0.3 mg.) was noted with ethylene glycol (a moderately viscous liquid) on both Botany flannel and jack shirting.

5. It was noted that penetration due to impact took place instantly if it took place at all. This contrasts with penetration under static conditions, which may sometimes require minutes or hours and always requires at least a sizable fraction of a second. Larger drops on impact invariably appear to be shattered, with parts of the drop either rebounding or sliding

off the surface. Only a portion of an impinging large drop is retained by the fabric for future static penetration.

Since it was of interest to explore further the relationship between fabric construction and penetrability in the impact test, a series of fabrics was tested using a single test liquid of relatively low viscosity, diethyl sebacate. The fabrics differed in air permeability, weight, cover, and stiffness and amount of nap or surface fuzz. The results are shown in Table X.

It is evident that there is relatively poor correlation between air permeability and impact penetration. Wool melton, cotton twill, and cotton denim have roughly the same air permeability, but the wool melton is more than 200 times as effective as either of the other two fabrics in resisting impact penetration. Similarly, the wool flannel has twice the air permeability of the tropical worsted, but it also has three times the resistance to impact penetration. There was also a lack of correlation between wicking and impact penetration resistance.

The determining factor in impact penetration resistance appeared to be the cover of the fabric. Both the wool melton and the 9-oz. sateen had excellent cover, allowing practically no pinpoints of light to shine through. The other fabrics showed a relatively large number of light-transmitting pinholes. The chambray, tropical worsted, T-shirting, and 80 × 80 print cloth had particularly poor cover and correspondingly high impact penetrability. The oil-and-water-repellent oxford fabric was essentially impermeable. It showed a few pinholes where the treatment had not been perfectly applied, and these pinholes were evidently responsible for trace quantities of liquid penetration which were observed.

Static Penetration vs. Impact Penetration

In the course of the impact penetration experiments described above, one of the fabrics tested was a material impregnated with a finely powdered solid. This material had good cover but it appeared to be highly absorbent and very easily wetted by the test liquid. Prior to the impact test a mandrel test had been carried out on this fabric. With a 20-mg. drop of diethyl sebacate it gave a weight penetration ratio of 1% in 1 min. at 0.25 lb./in.^{2} pressure. This is considered quite high. It was therefore quite surprising that in the impact test with a 20-mg. drop of diethyl sebacate no penetration whatsoever occurred, even after the liquid had had ample time to soak into the fabric. It soon became evident that the impact test differed from the static test in two important details. Part of the impinging drop is lost by spattering so that the quantity of liquid available for subsequent static penetration is smaller than the original impinging quantity. The area over which the impinging drop spreads is greater than the area over which the statically applied drop spreads. Quantitative determinations of the above factors were made, and the results are shown in Table XI.

Table XI, Section A, shows what happens to the charcoal fabric in the impact test. A 20-mg. drop

TABLE X. Impact Penetration of Fabrics by Diethyl Sebacate

21-mg. drop size. 40 miles/hr. impact velocity

Fabric	Air permeability, ft.^{3}/ft.^{2}/min. at ½-in. p.d.	Ratio, number of penetrations to number of hits	Wt. penetration ratio, %
Cotton chambray	146	1	9.0
Tropical worsted	40	1	6.7
11-oz. wool flannel	86	1	1.9
Cotton uniform twill	13	1	1.2
Cotton denim	24	1	1.0
16-oz. wool melton	20	0.5	0.005
9-oz. cotton sateen, repellent finish	5.3	1	0.005
9.5-oz. nylon fleece, pile side out	228	1	8.1
9.5-oz. nylon fleece, pile side in	228	1	7.2
Cotton T-shirting	310	1	10.5
80 × 80 cotton print cloth	103	1	12.0
5-oz. Botany flannel	125	1	6.0
14-oz. 85/15 wool/nylon Jack shirting	49	1	0.5
5.5-oz. cotton oxford, untreated	5.6	1	4.3
5.5-oz. cotton oxford, oil-and-water repellent	0.16	0.5	0.005

TABLE XI. Impact vs. Static Penetration Using Diethyl Sebacate

	Fabric					
	Charcoal-impregnated double-woven twill	9-oz. sateen	Cotton twill	Botany 404 wool flannel	9½-oz. nylon fleece, pile side out	9½-oz. nylon fleece, pile side in
A. *Impact conditions*						
Drop size, mg.	20	20	20	20	20	20
Amount lost by splashing and/or centrifugation, mg.	8	8	7	9	14	4
Amount retained on fabric, mg.	12	12	13	10	6	16
Area of splash on fabric, mm.²	113	115	154	140	30†	about 100‡
Mg. liquid/mm.² of fabric (surface density)	0.106	0.104	0.085	0.072	0.2	0.16
Penetration, %	0	0.005	1.3	6	8	7
B. *Static conditions*						
1. Liquid applied over large area						
Pressure, lb./in.²	0.25	0.25	0.25	0.25	0.25	0.25
Quantity of liquid applied, mg.	20	20	20	20	20	20
Area over which liquid was applied, mm.²	250	250	250	250	250	250
Mg. liquid/mm.² of fabric	0.08	0.08	0.08	0.08	0.08	0.08
Penetration in one minute, %	0	0	0.02	0	0	0
2. Liquid applied in drop form						
Pressure, lb./in.²	0.25	0.25	0.25	0.25	0.25	0.25
Drop size, mg.	20	20	20	20	20	20
Area wetted by the drop, mm.²	96	80	100*	112	28	100‡
Mg. liquid/mm.² of fabric	0.21	0.25	0.2	0.178	0.71	0.20
Penetration in one minute, %	1.0	8.0	5.0	0	30	0

* Initial area. Wet spot spreads to 250 mm.² in 1 min. Keeps spreading.
† Spreads over wide area (500 mm.²) on the reverse side of the fabric.
‡ Spreads to about 500 mm.² in 1 min. Keeps spreading.

impinges but 8 mg. of this drop is lost by spattering. The remaining 12 mg. is spread over an area of 113 mm.² The quantity of liquid per unit of fabric surface is 0.106 mg./mm.². *This is evidently too low a surface density to cause any static penetration subsequent to the impact.*

Table XI, Section B-2, shows what happens in the standard type of static soaking test described above. The 20-mg. drop as applied covers an area of 96 mm.² (this area varies by about ±10% at the time of application and it increases with time due to spreading) or 0.21 mg./mm.². This is a high enough surface density to cause penetration. In Table XI, Section B-1, the 20-mg. drop was spread on a steel block to an area of about 250 mm.² and was then transferred onto the fabric surface. In this case the surface density was 0.08 mg./mm.², close to the surface density obtained in the impact test, and no penetration occurred.

The remaining columns of Table XI show the results of similar sets of experiments on the 9-oz. cotton sateen, cotton twill, and Botany flannel. The sateen under standard mandrel test conditions showed a surface density of 0.25 mg./mm.² and allowed 8% of the applied liquid to pass. At a surface density of 0.08 mg./mm.² there was no penetration. Under impact conditions only 12 mg. of the 20-mg. impacted drop was retained, the surface density was 0.1 mg./mm.², and the penetration was negligible.

The nylon fleece fabric, a "synthetic fur" type of fabric with a knit backing and a tufted pile, behaved in an interesting and unusual manner. The smooth knit backing of this fabric showed an extremely rapid wicking action on the test liquid, diethyl sebacate. The pile side of the fabric, however, had no lateral wicking action. Under impact this fabric showed a very high penetration ratio regardless of which side faced the drop. This property corresponds with the

fact that the fabric has poor cover, allowing much light to shine through.

When the drop was applied to the pile side under static conditions the penetration appeared to be greatly influenced by the surface density. At a surface density of 0.71 the penetration ratio reached the exceptionally high value of 30%. At a surface density of 0.08 mg./mm.^{2} the penetration ratio was zero. Under impact conditions the surface density turned out to be 0.2 mg./mm.^{2} and the penetration ratio was 8%.

When the drop was applied to the smooth side under static conditions it wicked laterally at a rapid rate so that there was no penetration through the underneath pile to the paper substrate even at high initial values of surface density.

Summary

Test procedures and apparatus are described for measuring capillary, pressure, and impact penetrations of fabrics by small, isolated masses of liquid. Capillary penetration, which occurs solely as a result of capillary forces, and pressure penetration, caused by a slowly acting, external driving force, are similar in many respects. The major liquid property affecting these two types of penetration is the wicking power (which of course depends on the fabric and fabric finish as well as on the liquid). High wicking power results in a rapid diminution of the surface density, defined as the weight of liquid per unit superficial area of fabric wetted. At low surface density penetration tends to be correspondingly low. Fabric tightness and denseness have the expected influence on capillary and pressure penetration, but the most important fabric property appears to be the fuzziness, or the quantity and stiffness of nap. The fabrics most resistant to penetration have a nap long and stiff enough to prevent contact between the substrate and the liquid-laden yarns. The nap fibers are shaped and spaced to resist being easily compressed to a wicking mass capable of conducting liquid to the substrate.

Impact penetration is defined as the penetration resulting from a drop being thrown against a fabric with appreciable momentum. In this situation part of the liquid may penetrate instantly because of its momentum rather than being conveyed through the fabric by capillarity. Part of the liquid may also be dissipated by spattering. The major factor in resistance to impact penetration appears to be the cover of the fabric. Fabrics with good cover, i.e., few or no straight-through channels from face to back, show the highest resistance. Appropriately constructed fabrics may resist penetration by a rapidly moving drop better than they resist capillary penetration by a drop of the same size.

Acknowledgment

We gratefully acknowledge the help of Mr. Dimitri Stancioff, who made many of the measurements of penetration herein recorded.

Literature Cited

1. Gillespie, T., *J. Colloid Sci.* **13**, 32 (1958).
2. Minor, F. W., Schwartz, A. M., Buckles, L. C., and Wulkow, E. A., *Am. Dyestuff Reptr.* **49**, No. 12, 37 (1960); TEXTILE RESEARCH JOURNAL **29**, 931–939, 940–949 (1959).
3. Minor, F. W., Schwartz, A. M., Wulkow, E. A., and Buckles, L. C., TEXTILE RESEARCH JOURNAL **29**, 931 (1959).

Manuscript received September 30, 1960.

Wearing Qualities of Selected New Mexico Wools

Part I: Strength and Elongation[1]

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Abstract

Four lots of wool fiber, selected for fineness and crimp, were manufactured into comparable tropical worsted fabrics for wear in outer garments by girls six to 16 years of age.

Breaking strength and elongation were used to measure the changes in the fabrics with wear. The breaking strength of the warp and of the filling of the fabrics made from the fine wools was greater than for the medium wool. Loss in fabric strength was a linear function of the hours of wear. Fabric elongation decreased with hours of wear, but generally, in a less direct fashion than did the strength.

The backs of the garments and the filling yarns in the backs lost most strength and elongation with wear.

Introduction

For a number of years the quality of New Mexico fine wool, known on the market as Roswell fine wool, has benefited from the long-range breeding program of the New Mexico Agricultural Experiment Station. Progressive improvements have led to some superior fiber qualities; most noteworthy are length and fineness.

Recently, considerable attention has been given to the marketing of these wools. As a result, questions arise concerning the usefulness and desirability of specific fiber qualities. A number of laboratories have contributed to the information on relationships of fiber properties to the functional behavior of fabrics [8, 14]. Such studies help to establish a basis for improved market apraisal of fiber properties. By this means, better returns should accrue to the producer of wools with superior qualities. For example high crimp [4, 9, 11, 19, 21] is thought to be associated with certain desirable qualities of wool fabrics, but as yet it has not been evaluated in studies on wear.

The nature of natural crimp has been clarified by work which was carried out simultaneously in the laboratories of Mercer [15] and Horio and Kondo [11]. They demonstrated the bilateral structure of the entire length of wool fibers. Investigators in each instance concluded that differences in the stability of the two parts of the cortex of the wool fiber were responsible for the spontaneous coiling of a free single fiber and natural crimping of a mass of fibers as in a raw fleece.

From a study of force–extension curves on wool of different grades and sources, Evans [8] concluded that the cross-sectional area and crimp accounted for observed differences in mechanical properties of wool fiber.

In a comparison of wools between and within several breeds of sheep, O'Connell and Lundgren [18] concluded from stress–strain analyses of wet fibers that crimp in the fiber strongly influenced the mechanical properties. Menkart and Detenbeck [14] found that fiber crimp persisted through the various manufacturing stages to the fabric. They observed, among other things, that wools with high crimp produced tops with greater cohesion, performed better in spinning to yield a bulkier yarn, and gave a thicker fabric with a softer hand, smoother appearance, better drape, and better wrinkle recovery than the low crimp wools. However, they reported that there was no apparent effect of crimp on the tensile strength of the fabric. The high crimp wools were found to be the most hygroscopic.

[1] Journal series 152, Agricultural Experiment Station, New Mexico State University of Agriculture, Engineering, and Science.

From a study of apparel wools, von Bergen and Wakelin concluded that, so far as efficiency of manufacturing operations is concerned, fineness appeared to be the most important characteristic of the wool fiber [22]. Since fineness is considered to be a physical property of prime importance, it should be appraised for serviceability in the use of the end products [1, 5].

Because of the importance of crimp and fineness in the marketing and manufacturing of apparel wools, these properties were the basis for selection of the fine wools used in this study on changes in certain physical properties of fabrics made from them during wear and care.

Materials

Fiber

The selection of fiber lots can best be described by reference to some steps in the fine-wool crimp studies which were under way at the time [16, 17] and to a study on medium wools [12].

In 1954, 324 of the fine-wool fleeces were selected at random from 6000 ewes on an eastern New Mexico ranch and visually classified into six lots on the basis of crimp. After microscopic measurements of fineness were made, the six lots were combined (one and two, three and four, and five and six) to form three lots. Then for purposes of further work, a control lot was made up of each fourth fleece from each of the three lots. Therefore, two-thirds of the fiber in Lot 4 was of better crimp and finer than Lot 3, and curiously enough, the fiber in Lot 4 was shortest after combing. This may have been caused by poor performance of the blended wool on the cards. Lot 2, intermediate in crimp, was omitted from this study. Lot 1 was slightly the finest and contained the longest and best crimped fiber. Of the fine wools, Lot 3 was the coarsest and contained the poorest crimped fiber. However, differences in measured crimp ratio were non-significant. The fine wools, Lots 1, 3, and 4, were from basically Rambouillet stock.

One lot of medium wool, Lot 5, was added for comparison. Lot 5 was taken from a 1954 clip of Territory wool from a crossbred flock of basically Panama and Columbia breeding and used in a study on hairiness in medium wools [12]. These four lots of wool (1, 3, 4, and 5) used in this study were from "tub" or unsorted fleeces. Such fleeces are processed with no preparation other than removing the strings used to tie them.

The wool was scoured at the University of Wyoming, carded at the Agricultural Research Center of the United States Department of Agriculture, Beltsville, Maryland, and Noble combed at the Philadelphia Textile Institute. The quality of the tops was determined by the Wool Associates of the New York Cotton Exchange, Incorporated, Boston, Massachusetts, and were valued on the basis of the Wall Street Journal quotations for July 7, 1955. The market value of the tops was inconsistent with fiber properties of fineness and crimp. Data on the physical dimensions and value of the fiber lots are given in Table I.

Fabric

After the four lots[3] (1, 3, 4, and 5) were made into tops, sufficient yarn was spun from each lot to produce about 70 yards per fiber lot of a plain weave tropical worsted fabric. Warp and filling yarns were alike in each construction except for fiber composition which produced differences. Each fabric was designated according to its fiber content. Details

[3] Each lot of wool was carried through the manufacturing processes (top making, spinning, weaving, dyeing, and finishing) under the supervision of Percival Theel, Director of Research, Philadelphia Textile Institute.

TABLE I. Fiber Measurements

Fiber lot	Fineness [2]		Crimp [13]		Unstretched length, in.	Top value, $/lb.
	English* count	Diameter	Ratio width:depth	Visual group		
1	70's	20.01	3.17	II, Average	3.06	1.77
3	64's	20.61	3.59	III, Poor	3.00	1.79
4	70's	20.14	3.57	III, Poor	2.93	1.80
5	50's	30.29	Not measured—		3.06	—

* ASTM Designation: D419-58, "ASTM Standards on Textile Materials," October, 1959, p. 199.

TABLE II. Construction Details

Fabric	Yarns: Ply/size	Yarns: Strength, lb.	Yarns: Twist/inch, Singles "Z"	Yarns: Twist/inch, Ply "S"	Fabrics: Yarns/inch, Warp	Fabrics: Yarns/inch, Filling	Fabrics: Weight, oz./yd.²
1	2/40s	103.67	16	12.5	42	39	4.68
3	2/40s	97.33	16	12.5	43	39	4.47
4	2/40s	92.00	16	12.5	42	40	4.42
5	2/40s	90.33	16	12.5	41	39	4.66

of yarn and fabric construction as furnished by the manufacturer are given in Table II.

The four sets of yarns were spun on the American System, using the same machines for each set, and were woven into fabrics on the same loom. Manufacturing details were kept constant so that differences in behavior and appearance of the fabrics might be attributed to fiber differences. The slight unevenness which developed in the yarns from the 50's wool (Table I) was considered by the manufacturer to enhance the appearance of the fabric. The 50's fiber is not normally used in 40's yarn and produced some difficulties in spinning and weaving [20]. The finisher, however, liked the fabric.

The four lots of fabric were steam crabbed, scoured, then dyed in the same dye bath at boiling temperature. This was followed by a mothproofing treatment of Mitin FF at 160° F. After dyeing, the fabrics were tenter dried, sheared (back and face), pressed, decated, and sponged ready for cutting.

Garments

There were two problems to consider in the design of the wool jumpers to be made from the fabrics. The first problem was to provide a design which would allow satisfactory areas for sampling. The second problem was that all costs of manufacturing, alteration, and maintenance were to be kept to a minimum. Each garment was to be kept in repair and cleaned once each week during the time it was in use. The general appearance of the jumpers may be observed in Figure 1.

Fig. 1. General appearance of wool jumpers.

Standard pattern sizes were found to be of unsuitable proportions. Therefore, the girls who were to wear the jumpers were measured, then patterns were drafted for use. The patterns were tested in muslin for shoulder width and garment length. Girls were allowed to choose preferred lengths. As the girls put on and took off the muslin jumpers their movements were observed to determine structural points for reinforcing the wool jumpers. As a result, the armscye and neckline were corded and especially stitched. In order to avoid sagging and broken stitching at underarm seams, the fabric was edge stitched and the edges of the fabric overcast on an automatic machine. The side seams were then made with zig-zag stitch of zero length. Therefore, no repairs were necessary on any seams except for a few rips. The hems and belts, however, required frequent attention.

Wear Pattern

Each jumper was worn an average of 14 hr. per day for six days each week during the school year by girls six to 16 years of age at the Home of the Good Shepherd, a combination orphanage and mission school.

If a girl decided that the hemlines on her jumpers were too low or too high, adjustments were made accordingly. The length was a critical factor for older girls, and was the only source of garment alteration during the two years of wear. Probably, next of importance to the older girls was the tightness of their belts.

If for any reason a jumper was not worn as scheduled, the wearing time was extended until it had received the proper number of cleanings for the wear period in which it was scheduled to be withdrawn. When necessary, garments were reassigned.

The activities of the girls included painting furniture, cotton picking, rock picking, and baseball, as well as the more usual play activities and housekeeping and gardening duties. Belts were often used to line up personal supplies of bobby pins. Since the jumpers had no pockets, the girls took advantage of breaks in the stitching of hems to store chewing gum, candy, personal notes, and other treasures.

Cleaning and Care

A six-day wear schedule had two advantages. The girls could wear their own dresses one day each week to relieve the monotony, and timing was right for a regular weekly schedule of inspection, repair, and cleaning of the garments not being worn that week. Damage and repairs were plotted on Garment Outline Sheets for front and back.

Before cleaning all water or banana-oil soluble stains were removed. A modified Sanitone process (Commercial Standard CS 3-38) was used for all drycleaning. A satisfactory moisture content of the dry solvent was established by adding two ounces of water for each pound of wool garments. No other garments were cleaned with the experimental materials. The load was agitated for 35 min. in the cleaning solution, which was being circulated through a filter of diatomaceous earth at the rate of 2000 gal./hr. After being extracted for 3 min., and dried on hangers in a current of warm air for 30 min., the jumpers were folded front to back and flat pressed.

The jumpers were then ready for folding and ticketing with a Wear Record Sheet bearing the wearer's name and a code number corresponding to the one in the neck band of the garment. The wearers, with supervision and help as needed, kept daily records of the hours of wear per day.

Preparation for Sampling

After the jumpers were withdrawn from wear, they were given the usual drycleaning and pressing, but no further repairs. The hems and under-arm side seams were ripped, but not the shoulder seams. The garments were then recleaned and given a special rinse in a clear solvent. This time, the backs and fronts were pressed separately with a special effort being made to remove as much as possible of the wear-produced distortions in the fabrics. Each jumper was then folded back to front and stacked flat while waiting to be sampled.

Sampling

The extent of serviceability of fabrics, and especially of garments in actual use, is judged largely by individual subjective standards. Because it is the specific combination of durability and aesthetic properties of an apparel fabric which adapts it to its specific uses, a number of physical measurements were made. It seemed desirable to determine which of the tests would most effectively distinguish between fabrics made from fibers with different crimp and fineness, and which tests would best indicate the service given by the fabrics. Service as used here implies durability as well as the general appearance and hand of the fabric.

In order that approximately comparable areas of the fronts and backs of the different sized jumpers might be tested, sampling diagrams were used as shown in Figures 2 and 3. These diagrams were used in the preparation of the two sets of test specimens made from each of the 120 garments.

In addition, as a measure of new fabric uniformity, warp and filling specimens of breaking strength were taken at 20 intervals spaced throughout more than 60 yard lengths of each of the four fabrics.

The individual test specimens from the garments were prepared by drawing yarns and cutting to size.

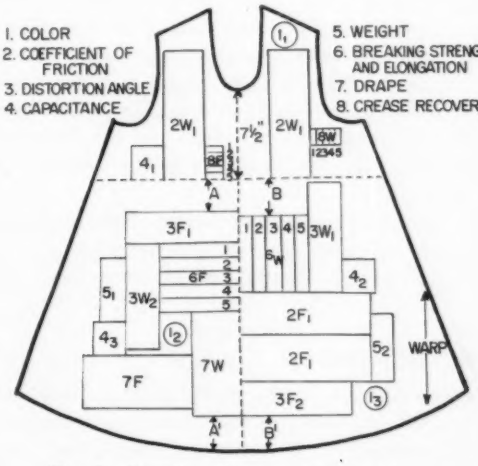

Fig. 2. Sampling diagram of front of jumper.

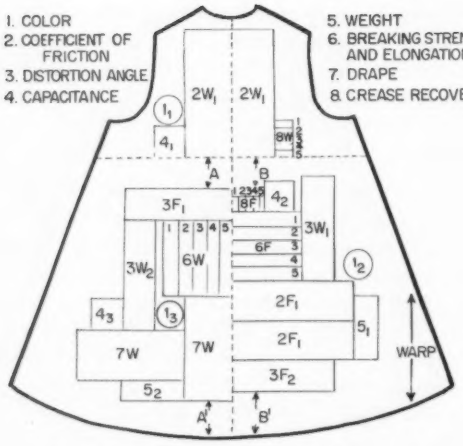

Fig. 3. Sampling diagram of back of jumper.

Consideration was given to stamping with a die, but this was found not to be feasible because yarns in the fabric had shifted during wear until useable test specimens could not, in most cases, have been taken. Measurements were made, yarns drawn, and specimens cut by hand. Even so, specimens such as those for distortion angle, coefficient of friction, and drape were difficult to handle.

Testing

Methods of testing, where possible, were from those outlined by Committee D-13 on Textile Materials [1]. Strength and elongation were measured on a Model J Scott Tester with an operating speed of 12 in./min. The number of warp and of filling yarns per inch of fabric was counted on sets of five 1-in. ravel-strip breaking-strength specimens. These data were used to calculate breaking strength per yarns as well as to provide an indication of shrinkage of the fabric during wear. This did not, however, compensate for yarn shrinkage in the direction of the test.

Elongation at break was calculated from the measurements made on the load–elongation chart as a percentage of the original 3 in. of fabric.

Procedures

Statistical Methods

Design of project. The statistical design was such that the hours of wear on the fabrics might accumulate most rapidly. Wearers were paired and each wearer was assigned two jumpers. One girl of each pair wore jumpers from Fabrics 1 and 3 while the other girl wore jumpers from Fabrics 4 and 5. That is, a pair of wearers wore jumpers from Fabrics 1 and 4 for six days of one week and from Fabrics 3 and 5 for six days of the next week. Garments were repaired and dry cleaned at the end of each six days of wear. These four jumpers constituted one replication of the fabrics. According to a predetermined random sampling plan, five replications were withdrawn at the end of each of the six wearing periods. There were 120 jumpers and 60 wearers in the study. Comparisons of progressive changes in properties of the fabrics with wear were thus made possible.

Analysis of data. Data were subjected to analyses of variance in order to assess the significance of variation among fabric means, among wear period means, and the fabric by period interaction with respect to the physical properties measured. Significant differences among fabric means at the 5% level of probability were determined by the application of Duncan's Multiple Range Test [7]. Linear and quadratic regressions were computed to characterize trends with respect to wear over a period of time. The orthogonal polynomial method was used to facilitate the regression analyses, and orthogonal coefficients were computed as described by Grandage [10] since garments were withdrawn at unequal periods in time. Coefficients of variation were computed for each analysis.

Results and Discussion

Breaking Strength

The four experimental fabrics designated as 1, 3, 4, and 5 were evaluated for breaking strength prior to any experimental procedures to which these fabrics were subsequently subjected. Each new fabric was randomly sampled at 20 intervals for strength in the warp direction and at 20 intervals for

TABLE III. Analysis of Variance of Breaking Strengths for New Fabrics

Source of variation	Degrees of freedom	Mean squares	
		Warp	Filling
Total	399	—	—
Fabrics	3	32,361**	1,146
Samples within fabrics	76	2,442**	2,466**
Determinations	320	96	337
C.V., %	—	1.62	3.19

** Denotes significance at the 0.01 probability level.

strength in the filling direction. Five breaking strength determinations were made for each sampling unit. The analyses of variance for these data are presented in Table III.

Differences among fabric means for warp breaking strength were highly significant ($P < .01$). The mean for Fabric 1 was 628.5 lb./1000 yarns, which was significantly greater than the means of the other three fabrics. Fabric 4 with a mean of 614.0 lb./1000 yarns was also stronger than Fabrics 3 and 5 with means of 589.8 lb./1000 yarns and 594.1 lb./1000 yarns, respectively. This order of strength for the fabrics is not the same as for the yarns (Table II). Mean warp breaking strengths for Fabrics 3 and 5 could not be statistically differentiated.

Filling breaking strength differences among the four unworn fabrics were non-significant and could be explained on the basis of random variability. Mean values obtained were 580.8, 578.9, 577.8, and 572.9 lb./1000 yarns for Fabrics 1, 3, 4, and 5.

Variation among samples within fabrics was highly significant for both warp and filling breaking strength, which indicates some heterogeneity in the materials under test. The coefficient of variability on mean warp breaking strength was lower than for the mean filling breaking strength (Table III).

The experimental fabrics were also evaluated after being subjected to various amounts of actual wear. Garments, made from the fabrics, were worn for specified periods of time. Five garments of each fabric were randomly withdrawn at the end of each of six wear periods. Five breaking strength determinations each for warp and filling were made on both front and back of each garment. The analyses of variance based on these data are presented in Table IV.

Variation among period means and variation among fabric means were found to be highly significant for warp and filling breaking strength for both front and back of the garments. The period by fabric interaction was non-significant for all cases, which indicates that the effects of these factors were independent with respect to breaking strength. Linear and quadratic regressions of breaking strength on periods of wear were computed, and in all cases the relationship could be expressed satisfactorily by a simple linear trend. Regression equations based on the mean breaking strength of the four fabrics and their corresponding r^2 values are as follows:

$$\text{Front warp } Y = 640.99 - 20.01X \quad r^2 = .98$$
$$\text{Front filling } Y = 616.46 - 32.32X \quad r^2 = .99$$
$$\text{Back warp } Y = 658.76 - 29.61X \quad r^2 = .97$$
$$\text{Back filling } Y = 638.14 - 42.57X \quad r^2 = .99$$

Y is the estimated breaking strength for a specified value of X, when X is the measure (coded) of the amount of wear before a sample was taken. The r^2 values, sometimes referred to as the coefficient of determination, indicate the amount of variation in mean breaking strength that was explained by the variation in periods of wear. The r^2 value for front warp, for example, is 0.98 which indicated that 98% of the variation in mean breaking strength was explained by periods of wear. The regressions based on individual fabrics are illustrated in Figures 4, 5, 6, and 7. Breaking strength decreased with wear more rapidly for filling yarn than it did for warp

TABLE IV. Analyses of Variance of Breaking Strengths for Fabrics in Worn Garments

Source of variation	Degrees of freedom	Mean squares			
		Front		Back	
		Warp	Filling	Warp	Filling
Total	559	—	—	—	—
Periods	5	191,544**	487,757**	422,273**	855,056**
Linear	(1)	935,214**	2,420,689**	2,044,610**	4,266,775**
Quadratic	(1)	5,606	4,710	53,798	9,778
Deviations	(3)	5,633	4,461	4,320	13,792
Error (a)	24	4,548	18,651	21,737	24,373
Fabrics	3	45,778**	128,436**	128,333**	234,473**
Period × fabric	15	2,177	6,611	8,644	19,339
Error (b)	72	1,540	7,076	5,437	17,520
Determinations	480	449	1,564	811	2,147
C.V., %	—	3.97	8.90	5.69	11.27

** Denotes significance at the 0.01 probability level.

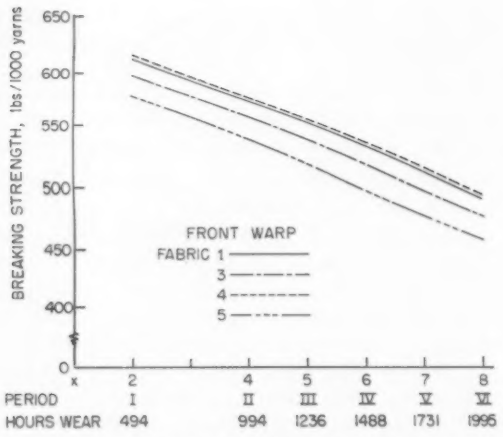

Fig. 4. Regressions of mean breaking strength on wear (coded) of front warp for four experimental fabrics.

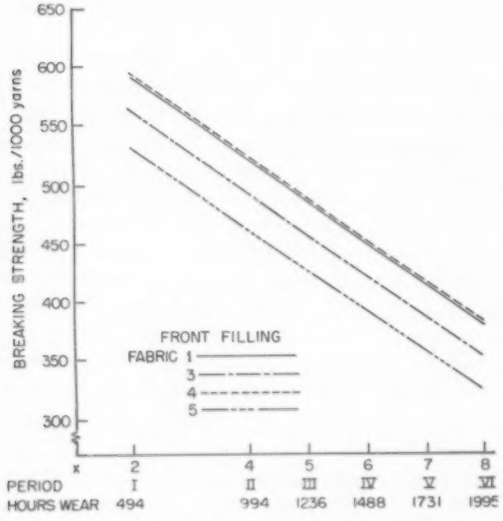

Fig. 5. Regressions of mean breaking strength on wear (coded) of front filling for four experimental fabrics.

TABLE V. Analyses of Variance of Breaking Elongation for New Fabrics

Source of variation	Degrees of freedom	Mean square	
		Warp	Filling
Total	79	—	—
Fabrics	3	52.23**	42.26**
Samples within fabrics	76	2.14	2.82
C.V., %	—	8.39	6.97

** Denotes significance at the 0.01 probability level.

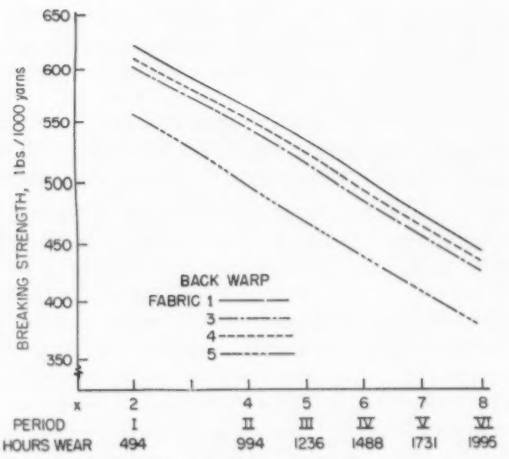

Fig. 6. Regressions of mean breaking strength on wear (coded) of back warp for four experimental fabrics.

yarns [6]. Likewise, it decreased more rapidly for the backs of the garments than it did for the fronts, as shown in Figure 8.

Fabrics 1 and 4 (see Appendix A) responded very much alike in all cases and mean difference in breaking strength associated with these two fabrics could be explained on the basis of random variability. Fabric 5 was consistently inferior with regard to breaking strength while Fabric 3 (see Appendix A) was always intermediate. Fabric 3 exhibited mean values which were significantly less than Fabrics 1 and 4 for front warp and front filling and Fabric 1 for back warp and back filling. Again coefficients of variability for warp were smaller than those for filling.

Elongation

Breaking elongation, expressed as a percentage of the original three inches of fabric clamped between the jaws of the strength machine, was measured to compare the four experimental fabrics when new and following a series of wear periods. Warp and filling for each new fabric was randomly sampled at 20 intervals and a single measurement of elongation was obtained for each sampling unit of five specimens. The elongations for a set of five warp specimens and five filling specimens were recorded on each Tensilgram. The analyses of variance for elongation of new fabrics are presented in Table V.

The breaking elongation of the four fabrics was quite similar for both warp and filling, although the

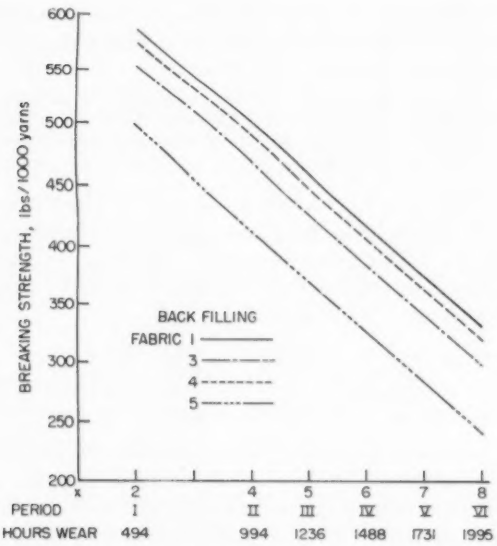

Fig. 7. Regressions of mean breaking strength on wear (coded) of back filling for four experimental fabrics.

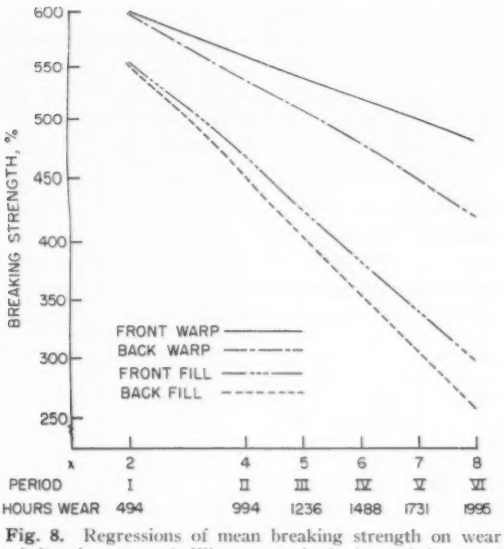

Fig. 8. Regressions of mean breaking strength on wear (coded) of warp and filling yarns in backs and fronts of the wool jumpers.

filling elongation was consistently higher. The warp elongation means for Fabrics 3 and 4 were 19.06% and 18.54% and were not significantly different. Fabrics 1 and 5, with means of 16.50 and 15.67, also could not be differentiated. However, the means of Fabrics 3 and 4 were significantly greater than the means of Fabrics 1 and 5. Fabric means for filling elongation followed exactly the same pattern. Means for Fabrics 3 and 4, 25.28% and 25.38% were significantly greater than the mean for Fabrics 1 and 5, 23.34% and 22.44%. Differences within these two groups, however, were non-significant and were attributed to random variability. Coefficients of variability were essentially the same for both warp and filling.

Evaluation of the fabrics with respect to elongation following wear was accomplished by taking measurements at the end of six wear periods. The analyses of variance for warp and filling elongation for both front and back of the garments are presented in Table VI.

The mean squares in Table VI show that highly significant variations resulted among periods and among fabrics for warp and filling elongation in both

TABLE VI. Analyses of Variance of Breaking Elongation for Worn Fabrics in Garments

Source of variation	Degrees of freedom	Mean squares			
		Front		Back	
		Warp	Filling	Warp	Filling
Total	119	—	—	—	—
Periods	5	76.63**	132.31**	118.61**	197.20**
Linear	(1)	334.00**	629.42**	524.63**	931.26**
Quadratic	(1)	.73	12.07	19.52	30.48*
Deviations	(3)	16.14**	6.69	16.30	8.08
Error (a)	24	3.14	4.58	5.88	5.69
Fabrics	3	117.14**	77.28**	117.10**	86.09**
Period × fabric	15	3.62**	1.79	4.05*	1.45
Error (b)	72	1.52	2.00	1.98	2.39
C.V., %	—	7.95	7.60	9.90	8.85

* Denotes significance at the .05 probability level.
** Denotes significance at the .01 probability level.

the fronts and the backs of the garments. In addition, period by fabric interactions were indicated for front warp and for back warp. Upon further analysis it was found that a highly significant quadratic by fabric interaction was the primary factor involved in the period by fabric interaction for front warp. This indicated that the association between breaking elongation and wear in the case of front warp was quadratic but the trends for each of the fabrics were not consistent. This prompted the computation of individual quadratic regressions for each fabric and prevented the use of a mean regression equation representing all fabrics. The following equations for front warp are given with their corresponding r^2 value.

Fabric 1	$Y = 18.86 - .1268X - .0619X^2$	$r^2 = .7639$
Fabric 3	$Y = 25.11 - 2.672X + .1778X^2$	$r^2 = .7913$
Fabric 4	$Y = 19.21 + .3139X - .1252X^2$	$r^2 = .9240$
Fabric 5	$Y = 18.86 - 1.732X + .0926X^2$	$r^2 = .8147$

The period by fabric interaction for back warp was accounted for by a linear period by fabric interaction. The linear regression equations for back warp elongation of the four fabrics and their corresponding r^2 values are listed below.

Fabric 1	$Y = 19.57 - .7962X$	$r^2 = .6198$
Fabric 3	$Y = 21.49 - 1.1556X$	$r^2 = .8821$
Fabric 4	$Y = 22.12 - 1.3428X$	$r^2 = .9079$
Fabric 5	$Y = 16.32 - .9462X$	$r^2 = .8289$

The period by fabric interaction was not indicated for filling elongation, which makes it possible to interpret trends on the basis of the means for the four fabrics. The linear mean square only was significant for front filling while linear and quadratic mean squares were both significant for back filling. The regression equations for these two cases and their corresponding r^2 values are as follows:

Front filling	$Y = 24.79 - 1.161X$	$r^2 = .95$
Back filling	$Y = 27.85 - 2.763X + .135X^2$	$r^2 = .98$

Regressions for breaking elongation with wear are presented in Figures 9, 10, 11, and 12.

The most striking result with respect to elongation was the consistently lower value found for Fabric 5. None of the other elongation means were significantly different except in the case of the front

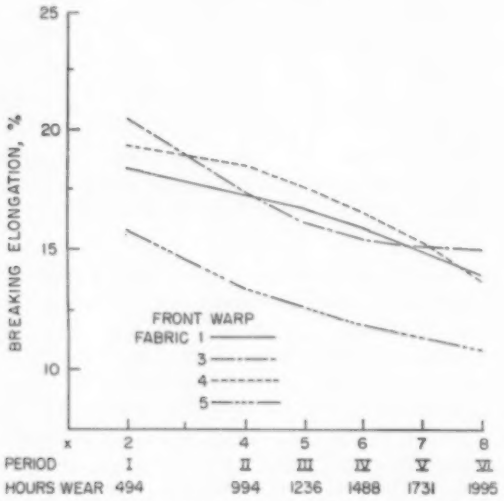

Fig. 9. Regressions of mean breaking elongation with wear (coded) for front warp of four experimental fabrics.

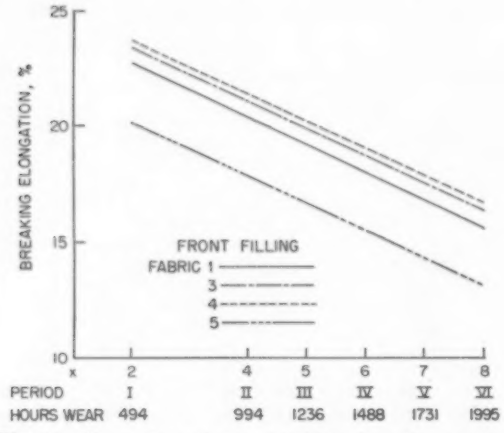

Fig. 10. Regressions of mean breaking elongation on wear (coded) for front filling of four experimental fabrics.

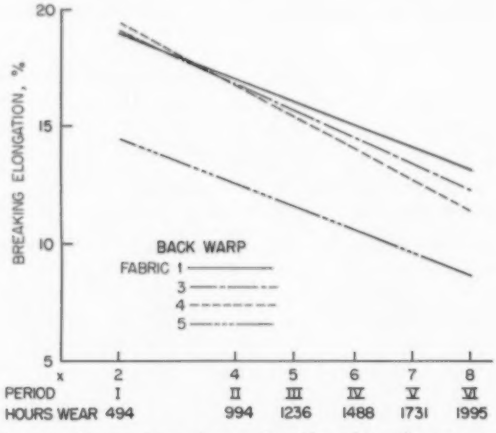

Fig. 11. Regressions of mean breaking elongation on wear (coded) for back warp for four experimental fabrics.

filling of Fabric 1 where the mean was found to be significantly lower than those for Fabrics 3 and 4. In general, the filling elongation tended to decrease more rapidly with wear than did the warp elongation. The backs of the garments also exhibited a greater rate of change in elongation than did the fronts of the garments.

Summary and Conclusions

In each of the four fabrics, yarns of the same fiber content and construction were used for both warp and filling. Therefore, differences in loss of fabric strength in the warp and filling directions of the backs and the fronts of the worn jumpers were considered to be the results of differences in wear on the two sets of yarns.

The breaking strengths of the warp yarns were higher than those for the filling yarns. The breaking elongations of the filling yarns were greater than those of the warp yarns.

The decrease in both fabric strength and elongation was more rapid in the filling yarns than the warp yarns. The decrease was more rapid in the backs of the jumpers than the fronts.

In general, the Fabrics 1, 3, and 4 from the fine wools tended to behave similarly and were significantly higher in both strength and elongation than Fabric 5 from the medium wool. The coefficient of variation tended to be greatest for the yarns with the greatest losses in strength and elongation.

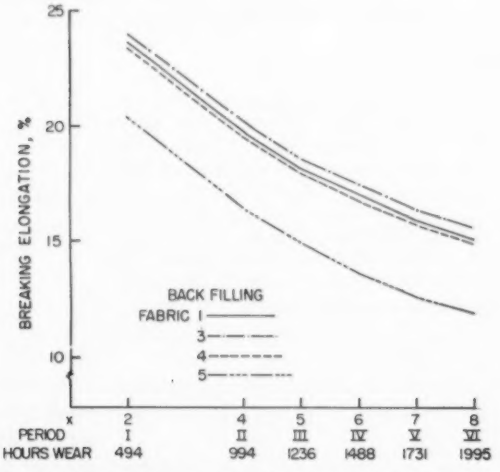

Fig. 12. Regressions of mean breaking elongation on wear (coded) for back filling for four experimental fabrics.

Acknowledgment

Thanks is expressed to the personnel and girls at the House of the Good Shepherd for their cooperation in wearing the jumpers and keeping the records on wear. Appreciation is expressed to the Quick Service Laundry and Cleaners for assistance in dry cleaning of the garments.

Literature Cited

1. American Society for Testing Materials, Committee D–13, "ASTM Standards on Textile Materials," Philadelphia 3, Pa. (1959).
2. American Society for Testing Materials, Committee D–13, "ASTM Standards on Textile Materials," Philadelphia, 3, Pa. (1956), ASTM

Appendix A

TABLE IA. Breaking Strength on Garments, Fabric Means*, Lb./Yarn × 1000

		Direction			
		Warp		Filling	
		Location			
		Front	Back	Front	Back
Fabric	1	546.8a	525.0a	466.5a	444.1a
Fabric	3	530.7b	505.7b	437.0b	410.9b
Fabric	4	548.5a	514.0ab	468.5a	433.6ab
Fabric	5	511.0c	458.6c	406.4c	355.5c
Mean		534.27	500.84	444.62	411.10
C.V., %		3.65	4.64	8.28	9.95

* Values followed by the same letter are not significantly different at the 5% level.

TABLE IIA. Breaking Elongation on Garments, Fabric Means,* Percentage

		Direction			
		Warp		Filling	
		Location			
		Front	Back	Front	Back
Fabric	1	16.18a	15.32a	18.74b	18.17a
Fabric	3	16.61a	15.33a	19.52a	18.72a
Fabric	4	16.84a	14.96a	19.85a	18.02a
Fabric	5	12.62b	11.27b	16.30c	14.97b
Mean		15.56	14.22	18.60	17.47
C.V., %		7.95	9.90	7.60	8.85

* Values followed by the same letter are not significantly different at the 5% level.

Designation D419–55T, "Tentative Specifications and Method of Test for Fineness of Wool."
3. Ashcroft, A. Griffin, TEXTILE RESEARCH JOURNAL **21**, 597–605 (1951).
4. Barach, J. L. and Rainard, L. W., TEXTILE RESEARCH JOURNAL **20**, 308–316 (1950).
5. Bouvet, René, *Ind. Eng. Chem.* **44**, 2125–2128 (1952).
6. Dowlen, Rowena P. and Ward, Ray L., TEXTILE RESEARCH JOURNAL **29**, 514–520 (1959).
7. Duncan, David B., *Biometrics* **11**, 1–42 (1955).
8. Evans, Thomas F., TEXTILE RESEARCH JOURNAL **24**, 637–643 (1954).
9. Evans, Thomas F. and Montgomery, D. J., TEXTILE RESEARCH JOURNAL **23**, 689–701 (1953).
10. Grandage, A., *Biometrics* **14**, 287–289 (1958).
11. Horio, M. and Kondo, T., TEXTILE RESEARCH JOURNAL **23**, 373–387 (1953).
12. McFadden, W. D., "Effect of Gare on Topmaking Qualities of Medium Wools," Agricultural Experiment Station, Bulletin 404, New Mexico State University, University Park, New Mexico (December 1955).
13. McFadden, W. D., Neale, P. E., and Finkner, M. D., "Influence of Crimp on Production and Combing Characteristics," Agricultural Experiment Station, Bulletin 382, University Park, New Mexico (November 1953).
14. Menkart, J. and Detenbeck, Jeanne C., TEXTILE RESEARCH JOURNAL **27**, 665–689 (1957).
15. Mercer, E. H., TEXTILE RESEARCH JOURNAL **23**, 388–397 (1953).
16. Neale, P. E. and McFadden, W. D., "Annual Report, Project WM–5," New Mexico Agricultural Experiment Station, University Park, New Mexico (October 1955).
17. Neale, P. E. and McFadden, W. D., "A New Method of Determining Crimp Quality of Fine Wool for More Accurate Grading of Fine Wool Clips," Press Bulletin 1080, Agricultural Experiment Station, New Mexico State University, University Park, New Mexico (March 1953).
18. O'Connell, R. A. and Lundgren, H. P., TEXTILE RESEARCH JOURNAL **24**, 677–685 (1954).
19. Rainard, L. W. and Abbott, Dorothea, TEXTILE RESEARCH JOURNAL **20**, 301–308 (1950).
20. Theel, Percival, Philadelphia Textile Institute, private communication, May 7, 1955.
21. U. S. Department of Agriculture, Western Regional Laboratory, Albany, California, "Report of Proceedings Technical Wool Conference," 15 (1951).
22. von Bergen, Werner and Wakelin, James H., TEXTILE RESEARCH JOURNAL **22**, 123–137 (1952).

Manuscript received October 10, 1960.

Effects of Tension During Resin Treatment on Physical Properties of Cotton Fibers and Yarns[1]

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Abstract

The effects of tension during resin treatment on the physical properties of yarns and fibers from the yarns were investigated on several cotton samples. The resins applied were of the melamine-formaldehyde and dimethylolethyleneurea types. The strength loss from slack treatments was the result of cross-linking of the internal fiber elements in unfavorable positions for stress equalization. Acid degradation was a factor in certain treatments. Low tensions during treatment were sufficient to prevent much of the strength loss. As elongation was reduced by tension, the energy to rupture was not greatly changed. The selection of high strength, high elongation cottons, and their premercerization increased the toughness. Tension before and during drying, followed by low tension during the cure, minimized the losses of toughness in yarns.

Introduction

A common practice in the processing of fabrics is to maintain limited control of fabric length and width by applying tension in the warp and fill directions. Tension is especially important during swelling treat-

[1] Presented at a meeting of The Fiber Society, October 27, 1960, Washington, D. C.

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ments not only to prevent changes in dimensions, but also to stabilize the effects on other properties. Tension during treatment has been shown to affect fiber and yarn properties in acetylation and other chemical treatments [3, 5, 7]. The effect of tension during resin treatment of cotton yarns is even more pronounced [6, 10]. The strength loss from resin treatment of slack yarns is largely restored by removing the resin. Treating under high tension causes permanent reduction in the X-ray angle with small loss in fiber bundle strength and large reduction in elongation [6, 8]. The changes in strength, elongation, and elastic recovery of cotton treated with bifunctional reagents, such as dimethylolethyleneurea (DMEU), which presumably cross-links cellulose chains and reduces slippage between fiber elements, have been compared to those resulting from monofunctional treatments, such as acetylation with monoethylolethyleneurea which does not cross-link [8].

The objectives of the present investigation were to establish the effects of tension during the processes of treating cottons with resin, on the strength, elongation, and elastic recovery properties as measured from the single fibers, fiber bundles, and yarns. Furthermore, it was desired to ascertain whether the decreases in strength and elongation were caused by the resin coating of fibers or by the bonding of internal fiber elements in positions unsuitable for achieving maximum strength. Finally, efforts were made to determine what combinations of chemical pretreatments, tension during treatment, and selection of cottons will improve the qualities of resin-treated fabrics.

Experimental

Samples

In order to determine the response of cottons of different fiber characteristics to resin treatment, several yarns of tex 37 :Z 476 × 3 :S 453 tpm (cotton 16/3) construction were selected. The yarns were from a high strength, high elongation cotton (Pima S-1); a high strength, low elongation cotton (Hopi Acala 50); a medium strength, high elongation cotton (Bobshaw); and a medium strength, medium elongation cotton (Stoneville 2B).

Treatments

Except as noted, pretreatments included a scour in 1.5% NaOH at 100° C. for 6 hr. Also, slack mercerization (20% NaOH followed by souring and washing thoroughly) was carried out on the scoured yarns before resin treatment.

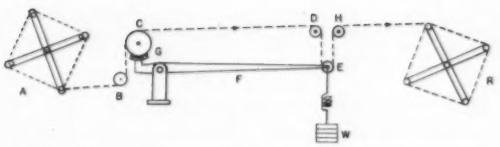

Fig. 1. Diagramatic sketch of yarn-tensioning apparatus.

Two commercial resins, methylated melamine-formaldehyde (MMF) and dimethylolethyleneurea (DMEU) were applied from solutions containing 9% by weight of the resin at 80% wet pick-up to give about 7% add-on of resin. The catalyst for the MMF resin was 0.5% hydroxyalkylamine hydrochloride and for the DMEU resin the catalyst was 0.5% modified zinc nitrate. All resin-treated samples were dried 10 min. at 50° C. followed by curing at 160° C. for 5 min.

The resin solutions were applied to skeins while slack, and the excess liquid was padded off before tension was applied. The yarns were then wound under controlled tension onto a reel of fixed dimensions as shown in Figure 1. While on the apparatus, the skein is held loosely on the holder (A). The yarn passes through a pretensioner (B) to a capstan type snub (C). After passing several times around the snub to achieve the necessary frictional grip, the yarn passes around pulleys (D), (E), and (H). The pulley (E) at the end of lever arm (F), actuates the brake (G) against the snub. The weight (W) is counteracted by the tension in the yarn except for the small force required to operate the brake. The reel (R) operates on a screw traverse to space the yarns regularly. The reel is easily detached for oven drying and curing the resin-treated yarn at a fixed length.

Measurements

Single-fiber and yarn tests were made with the Instron [4] tensile tester at a rate of strain to break the yarn within limits of 10 to 20 sec. Bundle tests were made with the Stelometer [4] [4] at a rate of loading of 0.5 kg./sec. and average breaking load controlled at 5.0 kg./sec. by adjusting bundle size.

[4] The mention of trade names does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

TABLE I. Single-Fiber, Bundle, and Yarn Strengths and Elongations for Pima S-1 Yarns Resin Treated to Approximately 7 Percent Add-on and Given an Afterwash

	Single fiber					Bundle			Yarn				
			Tenacity,*			Tenacity,*					Tenacity,*		
Treatment	Load at break, g.	Linear density, tex	g./tex	percent of control	Elongation, %	g./tex	percent of control	Elongation, %	Load at break, kg.	Linear density, tex	g./tex	percent of control	Elongation, %
Control	7.10	.138	51.3	—	12.9	28.3	—	10.9	1.84	72	25.5	—	11.7
DMEU slack†	3.34	.139	24.0	47	6.5	12.1	43	4.5	0.68	78	8.7	34	5.0
DMEU tension‡	4.09	.129	31.7	62	4.1	17.3	61	1.6	1.50	73	20.6	80	2.2
MMF** slack†	5.06	.139	36.4	71	9.4	13.0	46	4.8	0.90	77	11.7	46	5.6
MMF** tension‡	6.23	.129	48.3	94	5.0	23.5	83	3.2	1.74	74	23.4	92	2.9

* Gauge lengths: single fiber and bundles, 3.8 ± .2 mm.; yarns, 25.4 cm.
† 10 g. tension.
‡ 1500 g. tension.
** Methylated melamine-formaldehyde type resin.

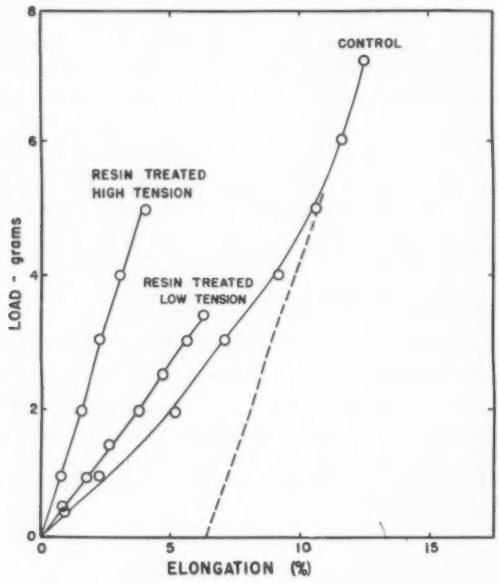

Fig. 2. Load–elongation curves for single fibers from DMEU resin-treated yarns.

Bundle measurements were made at zero and 3.2 mm. gauge (clamp spacings).

Results and Discussion

Properties of Fibers and Yarns

In investigations involving changes in the tensile properties of yarns or fabrics, information on the extent to which these changes result from changes in fiber properties is essential. Although data in this and previous investigations have shown that fiber bundle strengths and elongations must be the factors affected in order to cause changes in yarn strength and elongation, single-fiber measurements are essential to establish the degree to which the bundle properties represent those of fibers in aggregate. In Table I are given the tenacities and elongations of single fibers and bundles from resin-treated yarns and the corresponding properties of the yarns. Although appreciable differences among percent changes in single-fiber, bundle, and yarn tenacities are found, similar general trends were observed from each type of test. The resin treatment of slack yarn reduces tenacity and elongation significantly. However, tension during drying and curing prevents much of the loss in strength, but reduces elongation drastically. The changes in tenacity and elongation are illustrated in typical single-fiber stress–strain curves. In Figure 2 are plotted the average load–elongation curves for the ten most typical of one hundred fibers from DMEU-treated yarns. The slope of the load–elongation curve is essentially unchanged by treatment under low tension. Also, the loss in elongation is slightly less than the loss in strength. The slope of the load–elongation curve of fibers from yarns treated under high tension is relatively steep and about equal to that of the control at high load (dashed line).

Although single-fiber data allow a more complete understanding of fiber properties, the averaged single-fiber properties have limited meaning in a very variable fiber population. Yarn and fabric strengths, etc., are doubtless functions of properties of fibers in aggregates. From our present knowledge one must assume that a fiber in a yarn cross-section undergoes an elongation prior to break essentially equal to that of its immediate neighbors. Since fibers in a flat-bundle test undergo essentially equal elongations before break, it is probable that the bundle test measures the properties of fibers in aggregates effective in yarns or fabrics, provided the gauge length used in the bundle is equivalent to the average effective "grip length" between fibers in the yarn or fabric. Estimates of the effective grip length in yarns of untreated cottons derived from correlation of yarn strengths with bundle strengths at various gauge lengths [1, 4, 11], show that for predicting yarn strength, a bundle gauge length of about 3 mm. is better than one of zero gauge. In Figure 3 the relationship of bundle tenacity at 3.2 mm. gauge to yarn tenacity is shown for three of the cottons given scour and mercerization pretreatments and resin treatments at low and high tension. The higher average level of yarn tenacity in the group treated under high tension, forming line B, Figure 3, is probably the result of better alignment of the fibers in the yarns due to the high tension.

A high correlation between yarn and bundle elongations is evident from Figure 4. The upward turn of the curve is attributed to the increased angle of yarn twist in slack mercerization.

Effects of Tension on Fibers

The assumption that the large strength loss from slack resin treatment does not result from cellulose chain breakage alone is supported by the retention of strength with treatment under tension, and by the strength of slack-treated samples after the resin is removed. Strengths before and after treating and stripping are shown for yarns in Figure 5. In each the strength before stripping is shown by the solid line, A. After stripping the resin with 1.5% phosphoric acid, 5% urea solution for 1 hr at 80° C., the strengths, as shown by the dashed lines, B, of the controls and the samples treated with MMF are essentially equal. The resin-treated samples, as well as the controls, lose strength from the acid stripping, although the possibility exists that the resin has a slight protective effect. The dotted lines, C, show

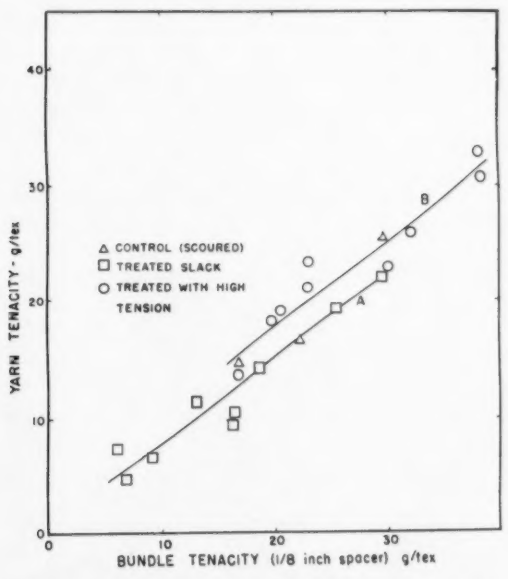

Fig. 3. Relationships of yarn to bundle tenacity for three pretreated cotton yarns, treated with MMF resin and cured at low, A, and high, B, tensions.

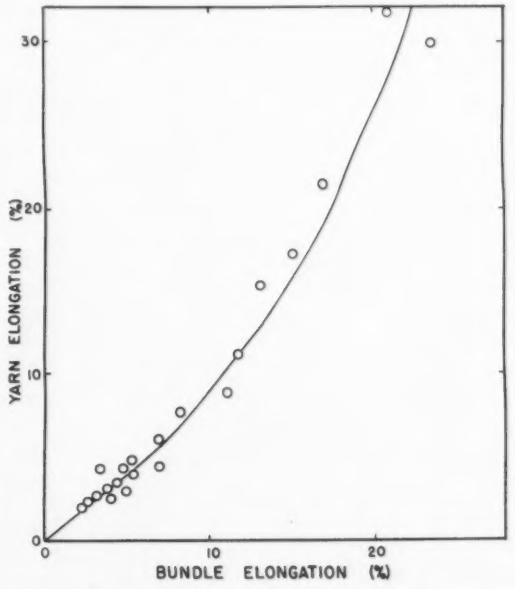

Fig. 4. Relationship of yarn to bundle elongation for several pretreated cotton yarns, treated with MMF resin and cured at low and high tensions.

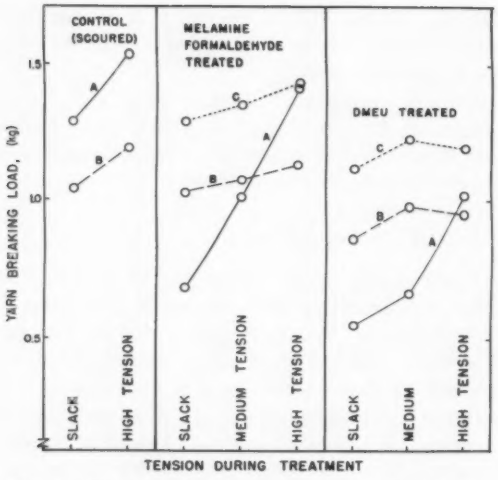

Fig. 5. Strengths of untreated and resin-treated yarns before, A, and after, B, stripping resins from yarns cured while slack and under medium and high tensions. Yarn strengths adjusted for stripping losses, C.

the strengths adjusted for the stripping-bath loss by assuming the same percent loss in the resin-treated samples as in the controls. The yarn breaking strengths found in these and other studies have indicated that chain breakage was less in the MMF treatment than in this particular DMEU treatment.

Effects of Tension on Yarns

The effects of tension during treatment on tensile properties were investigated in more detail for those yarns treated with DMEU than for those treated with MMF. When yarns were dried and cured at various tensions from 100 g. to 2000 g., the effects on strength and elongation are most pronounced at low loads, as shown in Figure 6. It is generally agreed that such resins increase the bonding forces between microscopic and submicroscopic elements of the fiber, which ordinarily slip past each other at relatively low tensions. The bonding forces are, in general, lateral to the cellulose chain molecules, which are more or less aligned with the fiber axis. On initial drying when the boll opens or after drying from subsequent wettings, the various structures in the fiber (chain molecules, fibrils, growth layers) are not necessarily in the best position to bear equally a load imposed on the fiber. The ability of these structural elements to adjust and support the load more uniformly is determined to a large extent by the lateral bonding forces. For a given length of structural element, lateral bonding of optimum strength must exist for maximum fiber strength. If the lateral bonds are too weak the whole element will slip; if they are too strong, the element cannot slip enough locally to allow equalization of tensions between elements.

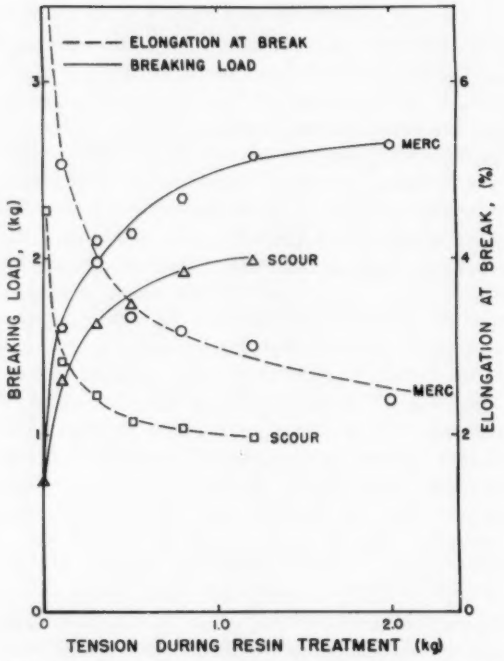

Fig. 6. Effects of tension during treatment on breaking load and elongation at break of scoured and mercerized yarns treated with DMEU resin.

In addition to the above factor, any nonalignment of the elements with the fiber axis introduces a strength loss which is proportional to $1 - \cos\theta$, where θ is the angle of the element relative to the fiber axis. This nonalignment must be taken into consideration in cotton fibers where the helix is not completely straightened before rupture. In slack resin treatment the strength loss attributed to this factor is insufficient to explain the total loss. Evidently the strength loss is due mainly to strong cross-bonds which prevent equalization of tension in the elements. A low tension in the fiber during treatment is needed to allow sufficient equalization of tensions so that the strong lateral bonding does not cause large strength losses. As one would expect, this low tension also reduces elongation.

An exact theory to account for fiber strength after

resin treatment under various tensions requires a greater knowledge of fiber structure, bonding forces, etc., than is available at present. The changes in strength and elongation shown in Figure 6 are, to a first approximation, exponential functions of the tension during treatment.

The practical advantages accruing from gains in strength due to applying tension during treatment are counteracted by the loss in elongation at break. The ability of textile fibers to withstand wear depends to some extent on both properties. Their product, which is related to the energy to rupture, or toughness, is frequently used as a measure of "wearability" of otherwise comparable materials. In Figure 7 are given toughness indices (one-half the product of strength and elongation) for several scoured cotton yarns treated at various tensions with MMF and DMEU resins, and in Figure 8 indices for yarns, pretreated by slack mercerization, also at various tensions during the MMF or DMEU treatment. As evident from comparison with the relationships shown in Figure 6, relative toughness is much less sensitive to tension during cure than either strength or elongation at break. The relative toughness of the untreated yarns ranges from about 75 for the Bobshaw and Stoneville samples to about 150 for Pima S-1. One might predict that the more elastic resin-treated samples will wear better under most circumstances than untreated samples of comparable toughness. The toughness value of 50 has been marked on the graphs for convenience in comparing samples. These results are for resin add-ons possibly above the level normally found in commercial applications, especially the DMEU resin, and thus cannot be used to compare the resins. The lower relative toughness of DMEU-treated yarn is attributed partly to greater acid degradation from the catalyst used and partly to the higher cross-linking efficiency of DMEU than of MMF at comparable add-on. Only in material not subjected to severe wear conditions can toughness be a secondary consideration in wash–wear treatments. However, toughness was highest in the cottons selected for high original strength and elongation. Also, slack mercerization prior to resin treatment increases toughness when compared on a basis of equal resin pick-up, but the greater accessibility of sites in mercerized cotton may require a slightly greater add-on to achieve the desired resilience.

The principal objective in applying resin to a fabric is to secure wrinkle resistance, which depends to a large extent upon the elastic recovery in the fibers. The extreme variability among cotton fibers makes quantitative measurements of elastic recovery made on single fibers very difficult. In these investigations elastic recovery was measured on the low twist yarns

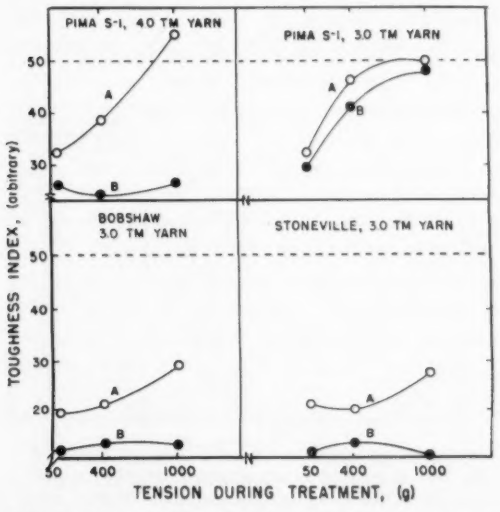

Fig. 7. The effect of tension during treatment with MMF, A, and DMEU, B, on toughness index for scoured yarns of Pima S-1, Stoneville, and Bobshaw cottons.

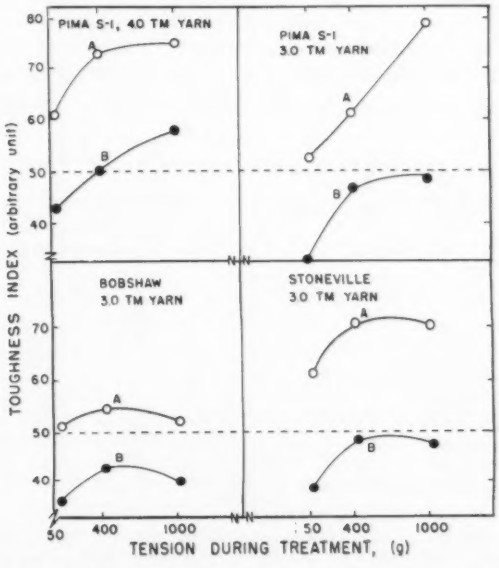

Fig. 8. The effects of tension during treatment with MMF, A, and DMEU, B, on toughness index for mercerized yarns of Pima S-1, Stoneville, and Bobshaw cottons.

using a modification [7] of the technique of Susich and Backer [9]. Typical recovery diagrams for scoured and resin-treated yarns are shown in Figure 9a and for the mercerized yarns in Figure 9b. In these plots the A curves are the load–elongation curves, the dashed curves, B and C, separate the elongation into immediate recovery, IR, delayed recovery, DR, and permanent set, PS. The permanent set measured at various stresses and strains is an indication of the lack of elastic recovery in a material. Slack mercerized yarn is very elastic at 2% elongation where many resin-treated samples show some permanent set. However, at 1-kg. load the permanent set in the slack mercerized yarn is already high, although in the resin-treated yarn it is negligible. The high permanent set of premercerized resin-treated samples is attributed to the greater accessibility of mercerized cotton. The mercerized samples may require higher resin add-on than the less accessible untreated cotton in order to attain equivalent resilience.

The samples discussed above were dried and cured on the reel at a constant strain throughout the process. There is, however, both academic and practical value in finding the stage of treatment at which the application of tension brings about the most desirable properties in the cottons. In Table II are given the strengths, elongations, and energies to rupture of yarns treated with about 8% MMF resin when tension was applied at various stages of treatment. The tension preceding and during drying is very important in the strength and elongation changes. Tension after drying slack caused no appreciable increase in strength over that of the slack treatment. The maximum energy to rupture was found in yarns tensioned while moist then dried and cured while slack. Moisture decreased slightly while yarns were under tension. The energy to rupture of these is significantly higher than that of either the sample tensioned throughout the treatment or the one treated slack throughout.

Since the resins are normally applied as solutions to the yarns, some migration of the reagent is possible during drying. The migration may be either along the yarn or to the surface of the yarn or fiber. The migration of MMF was followed qualitatively by staining with a 1% solution of Kiton Pure Blue V buffered to pH 3.0 [2]. Even with slow drying, samples dried under tension showed appreciable migration to the surface in the plied yarn. The samples dried slack showed the least migration, but the fiber cross-sections usually showed migration to the fiber surface. Any such nonuniformity would be expected to reduce both resilience and strength as compared to a uniform treatment. Also, the strength loss could result from reduced efficiency of cooperation among fibers in the yarn, or among fibrils in the fiber because of variations in elongation resulting from nonuniform treatment. This appears to be only a minor factor since samples uniformly treated while slack also show large strength losses.

Limited studies of the effect of tension applied during the treatment of fabrics rather than yarns show that tension has much less effect on properties

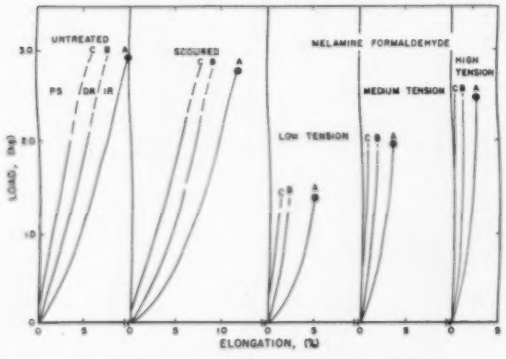

Fig. 9a. Load–elongation diagrams showing elastic recovery properties of scoured and MMF-treated yarns of Pima cotton. A, load–elongation curve; curves B and C, divisions of elongation into immediate recovery, delayed recovery, and permanent set.

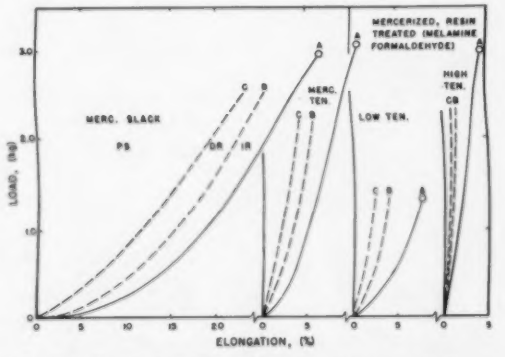

Fig. 9b. Load–elongation diagram showing elastic recovery properties of mercerized and MMF-treated yarns of Pima cotton. A, load–elongation curve; curves B and C, divisions of elongation into immediate recovery, delayed recovery, and permanent set.

TABLE II. Pima S-1 Yarns Treated with Methylated Malamine-Formaldehyde Type Resin with Tension Applied During Different Stages of Drying and Curing Processes

Treatment	Load at break, kg.	Elongation at break, %	Energy to rupture,* kg. in.
Control, slack (catalyst only)	2.71	11.5	1.07
Control, high tension† (catalyst only)	2.84	6.8	.73
Resin treated‡			
Dried slack, cured slack	1.44	5.5	.27
Dried slack, tensioned, cured slack	1.84	4.0	.28
Dried slack, cured under tension	1.76	3.6	.24
Tensioned, dried slack, cured slack	2.43	4.4	.41
Tensioned, dried slack, cured under tension	2.52	3.1	.33
Dried under tension, cured slack	2.56	2.6	.29
Dried under tension, cured under tension	2.66	2.2	.26

* Instron integrator values.
† 1500 grams initially.
‡ Approximately 8% add-on; mild afterwash.

of the fabric than it had on those of the low twist yarn. Even in fabrics treated while slack the fibers are under stress, especially when drying from the swollen state. High tensions in both warp and fill directions were difficult to achieve. However, in several fabrics with unequal tension in warp and fill directions, the reagents migrated to the yarns with the lower tensions.

Conclusions

Strength and elongation changes due to resin treatment of yarns are a result of strength and elongation changes in the fibers. The loss of strength in the slack treatment is caused principally by the cross-linking of the internal fiber elements in positions unfavorable for bearing equally the load on the fiber. Although application of even a low tension during treatment tends to reduce the strength loss, there is further loss in elongation. Energy to rupture of the tension-treated yarn is only slightly improved over that of the slack-treated yarn. The use of high strength, high elongation cottons and premercerization partially offsets the low toughness achieved for average cotton. Application of tension before drying followed by a low tension during the cure also minimizes the loss of toughness in yarns.

Acknowledgments

The authors wish to express their appreciation to J. J. Brown for the processed yarns; to R. M. Reinhardt and J. G. Frick, Jr., for aid in resin applications; to Ines V. deGruy for the staining tests for resin migration; and to Ruby H. Tsoi for statistical calculations.

Literature Cited

1. Brown, H. M., TEXTILE RESEARCH JOURNAL **24**, 251–260 (1954).
2. deGruy, I. V., *Sci. Monthly* **68**, No 1, 61–65 (1949).
3. Grant, J. N., TEXTILE RESEARCH JOURNAL **26**, 74–80 (1956).
4. Hertel, K. L. and Craven, C. J., TEXTILE RESEARCH JOURNAL **26**, 479–484 (1956).
5. McDonald, A. W., Orr, R. S., Humphreys, G. C., and Grant, J. N., TEXTILE RESEARCH JOURNAL **27**, 641–648 (1957).
6. Orr, R. S., DeLuca, L. B., Burgis, A. W., and Grant, J. N., TEXTILE RESEARCH JOURNAL **29**, 144–150 (1959).
7. Orr, R. S., Burgis, A. W., Creely, J. J., Mares, T., and Grant, J. N., TEXTILE RESEARCH JOURNAL **29**, 355–363 (1959).
8. Orr, R. S., DeLuca, L. B., Burgis, A. W., and Grant, J. N., in process of publication.
9. Susich, G. and Backer, S., TEXTILE RESEARCH JOURNAL **21**, 482–509 (1951).
10. Tripp, V. W., Orr, R. S., Ziifle, H. M., and Conrad, C. M., TEXTILE RESEARCH JOURNAL **28**, 404–417 (1958).
11. U S. Agricultural Research Service, Field Crops Research Branch, "Progress Report on the Annual Varietal and Environmental Study of Fiber and Spinning Properties of Cottons, 1954 Crop," Beltsville, Md., 83 pp. (June 1955).

Manuscript received October 26, 1960.

Quantitative Investigation of the X-Ray Diffraction Picture of Some Typical Rayon Specimens, Part I

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Abstract

The X-ray diffraction pictures of some typical specimens of highly orientated rayon are studied quantitatively using a diffractometer technique with Geiger counter detection and strictly monochromatized radiation.

The results allow of a more reliable separation between crystalline interferences and background than heretofore possible. The background of orientated rayons is anisotropic and has a complicated intensity distribution. It has maxima at about $2\theta = 21°$ on the equator and at about $2\theta = 35°$ on the meridian.

Evaluation of the intensities of the principal paratropic and diatropic interferences reveals about the same relative differences in crystallinity between the rayons investigated as those given by the method of crystallinity determination employed earlier. Absolute values of the crystalline fraction could not, however, be derived from the present work.

The relative intensities of the principal crystalline interferences are measured and found to be in reasonable agreement with those calculated for the Andress lattice structure. Some typical deviations are specified.

The crystallinity of tire cord rayon was found to be somewhat lower than that of textile rayon and the crystallites in the former somewhat smaller in lateral dimension according to measurements of line width. In the series of specimens investigated there is a correlation between crystallinity and line width. It seems that higher crystallinity tends to go parallel with larger or more perfectly ordered crystallites, a correlation which is also reported to have been observed in other polymers.

It is shown that orientation derived from the azimuthal spread of either the diatropic or the paratropic interferences leads to equal results. This is in support of the method developed earlier for quantitative determination of orientation from the paratropic lines in simple exposures on flat film.

The outcome of this kind of orientation measurement is but little, almost negligibly, affected by the error involved in assuming the background maximum to lie at the minimum between the A_0 and A_2 peaks and thus at a lower angle and at a slightly higher intensity than the true values.

1. Introduction

In the course of the last 15 years several studies on the X-ray diffraction of cellulose fibers have appeared from this laboratory. In particular, application of quantitative methods in the evaluation of diffraction pictures has been aimed at. The principal contributions of this kind have been: (1) determination of the orientation of the crystallites [5, 6, 8a, 16]; (2) determination of "crystallinity" [8a, 8b]; (3) determination of "scattering power" in the small angle range in absolute units [4, 13].

The present paper is concerned with another quantitative study of diffraction at wide angles, using a new technique. In this connection we shall very briefly recapitulate the first two of the subjects above, on which this investigation has a bearing.

In both cases the essential step is an attempt to separate the diffraction due to the crystalline portion of the specimen (e.g., the crystalline interferences or peaks on the photometer curves) from the diffuse

[1] Communication No. 110.

"background" appearing in all cellulose exposures. Admittedly, this has always been a somewhat arbitrary procedure; it has been adopted, however, by various workers, who were quite conscious of this fact, for lack of better methods [10, 16].

In the case of cellulose II, the background has been drawn diagrammatically as shown in Figure 1, which represents a photometer recording over the equator of the diagram. In other words, it has been assumed that the minimum between the A_0 (101) interference and the peak of the combined A_3 and A_4 (101 and 002) interferences is part of the background line. This implies that there is complete separation of the two peaks (without overlap) which—in absence of further evidence—is a mere assumption. That an error is actually introduced in this way will be demonstrated in the present paper.

Our earlier orientation measurements were based on exposures of oriented fibers on flat film in a fiber camera of the Astbury type. The usual conditions were Ni-filtered Cu-radiation, pinhole collimation (divergence of primary beam 0.86°) [5]. Under these conditions (and apart from some artificial line broadening due to divergence of the primary beam) the diagrams obtained by photometration of the film are distorted by two "parasitic" phenomena:

(a) radiation scattered by the air in the camera and
(b) the nonmonochromatic components of the Ni-filtered radiation ("white radiation").

The background line in diagrams of this kind, when drawn as exemplified in Figure 1, is severely off its true shape, which would appear if the "parasitic" components of scattering were eliminated, as illustrated in a preceding paper [9]. However, as far as orientation measurements are concerned (implying only measurements of the height of the peaks above the background) no significant additional errors are introduced by the parasitic radiations [9]. Therefore, simple Astbury-camera exposures with Ni-filtered radiation may be used in this case.

In the case of "crystallinity determinations" (determinations of the "crystallinity index" as proposed by A. Wuorinen based on the same principle [23]), it is essential to exclude parasitic radiations. Conditions were: Cu radiation monochromatized by reflection at a crystal face, pinhole collimation (divergence of primary beam 1.8°), fiber sample consisting of a completely randomized isotropic specimen, a flat film. Corrections for air scattering and incoherent radiation were applied. Furthermore, means were provided to measure the relative intensity of the primary beam and the absorption by the specimen in order to make possible normalization of intensity measurements on exposures of different specimens [11].

Despite the precise techniques of exposure, the method involves several sources of error. It requires isotropic specimens which give rise to "powder diagrams" with sacrifice of many details of the crystalline interferences. The projection of the diffracted radiation on a flat film entails distortion of relative intensities in a function of the angle of deviation and requires corrections of a not always quite certain nature.

To the authors' knowledge, the true intensity distribution in X-ray diffraction pictures of oriented fibers has thus far not been thoroughly examined quantitatively by correct techniques. The present investigation is an attempt to fill this gap to some extent.

2. Experimental

The apparatus used was a Philips diffractometer designed for transmission, combined with a stabilized X-ray tube with copper target. The constancy of the radiation from this source was checked throughout the work.

In the diffractometer a beam collimated by a horizontal slit (aperture about 1°) is passed through the sample on the specimen holder, which can be automatically rotated around a horizontal axis. The diffracted radiation was detected by a single-chamber Geiger counter mounted on a bracket rotating around a horizontal axis with twice the angular speed of the sample. The Geiger tube is switched to a Philips electronic counter unit and recording potentiometer, delivering a plot of intensity versus scattering angle.

The specimen consisted of a compact pad of fibers wound parallel on a specimen holder which can be positioned with the fiber axis at any angle from the horizontal. In this way radial intensity recordings can be obtained at any azimuthal angle. In fixing the mechanism at a preselected angle of scattering, 2θ, and automatically rotating the specimen holder in the plane of the specimen, azimuthal intensity recordings can be also obtained at any scattering angle.

As an essential improvement to the device, the rays falling on the Geiger tube were monochromatized in a quartz bent-crystal monochromator mounted before the Geiger counter on the moving diffractometer bracket and focused on the entrance aperture of the counter [22]. An adjustable slit opposite the crystal permitted adjustment of the aperture.

The constancy of the primary intensity was frequently checked by measuring the intensity diffracted by stand-

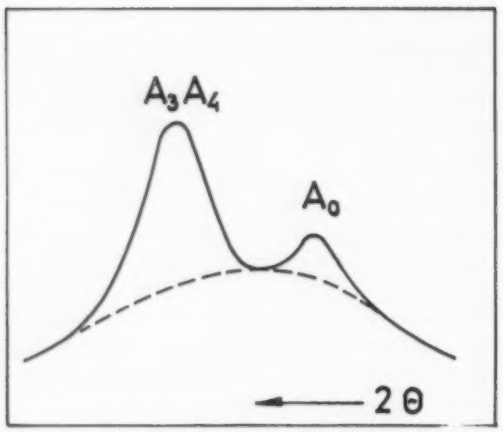

Fig. 1. Typical equatorial photometer curve of a rayon specimen (diagrammatic); broken line represents conventionally assumed background.

ard samples consisting of plexiglass plates at $2\theta = 13.5°$ (locus of an intensity maximum). Several such standard samples were kept in stock in case of possible deterioration of the frequently used one by X-ray exposure. In this way corrections for (small) daily intensity variations could be applied. All intensity measurements were corrected for non-linearity of the detection and recording device, when required [15]. By checking the equatorial recordings of one rayon sample at various primary intensities and with differing recorder sensitivity, it was made sure that the equation used for non-linearity correction actually applied within the range of intensities recorded. The corrections were always smaller than 20%.

3. Normalization of the Intensity Measurements

For every fiber specimen the absorption was measured. From the equation, $I/I_0 = \exp[-\mu d]$, the μd value of the specimen was determined. (I_0 and I are the intensities without and with the specimen in the beam, μ is the linear absorption coefficient, and d is the thickness of the specimen.)

In order to normalize all intensity measurements to one and the same (arbitrary) unit of intensity, the following factors were accounted for: intensity of primary beam during the experiment; optical density (μd value) of the specimen; oblique incidence on the specimen when positioned at an angle θ to the primary beam. If any recorded intensity (after correction for non-linearity) be I, then the normalized intensity is

$$I_n = \frac{P_s}{P} \cdot \frac{1}{e^{-\mu d/\cos\theta} \cdot \mu d} \cdot I \qquad (1)$$

(Compare Compton and Allison, "X-rays in Theory and Experiment," second edition, New York, Van Nostrand, 1935, p. 418.) P_s = accepted fixed value of the corrected intensity recording of the standard sample in arbitrary units, P = corrected intensity recording of the standard sample at the experiment in question. The value of $\exp[-\mu d/\cos\theta]$ was taken from calculated plots.

Since the experiments were performed in air, there was also a contribution of air scattering to the intensity recordings. As is well known, this contribution is strongly dependent on the scattering angle, 2θ. All intensity recordings were corrected for air scattering. This was done by means of a "standard air-scattering curve" recorded as a function of 2θ without a specimen in the beam.

If $I\ (2\theta)_{air}$ is the intensity of the standard curve at the angle 2θ, then the intensity to be subtracted from a recording with a specimen in the beam is

$$\frac{P}{P_s}\left[I(2\theta)_{air} + k\right] e^{-\mu d/\cos\theta} \qquad (2)$$

where k is a constant for the given experimental setup (related to the so-called "zero effect" of the counter). It amounted to 0.185 in our case.

This correction is subtracted from the actual recordings before normalization of the intensities. It usually became negligible beyond $2\theta = 20°$ but was very important at $2\theta = 5°$, where our recordings started. There it amounted to 10–50%, or even more, of the recorded intensity, depending on sample thickness.

4. Specimens Investigated

For this work some typically representative rayon fibers were selected. A brief characterization of each is given here, along with the code numbers from our records.

704 "Fiber G," an experimental viscose rayon obtained by courtesy of Du Pont de Nemours, Wilmington, Del. This rayon is known for high orientation and unusually high crystallinity and has been previously used by several other authors as well as by ourselves in investigations on rayon.

705 A highly oriented viscose rayon spun from alkali-rich viscose in a two-bath process with 80% stretch. This rayon can be classified as a "common textile rayon" of relatively high tensile strength. Its crystallinity, according to the classical X-ray evaluation, has a value characteristic for the majority of rayons. (Designation: textile rayon.)

706 A fiber typical of the class designated as "tire cord rayons," spun according to a special procedure and

with a typical "modifier" in the bath. It has high orientation and high tensile strength and fatigue resistance. Its crystallinity could not be determined by the classical evaluation method owing to bad separation of the A_0 and A_2 interferences (due to the presence of a certain fraction of the modification cellulose IV in the crystalline portion of the fiber. (Designation: cord rayon.)

707 A cuprammonium rayon of American origin, spun by the classical funnel process. (Designation: cupr. R.)

709 "Fiber G" which had been subjected to a "mercerization" (10-min. dip in 18% by weight aqueous sodium hydroxide followed by dip into boiling 0.5% acetic acid; fibers held under constant length throughout). (Designation: mercer. Fiber G.)

5. General Method of Evaluation of the Diffraction Picture

It was our aim to study the diffraction pattern given by some typical specimens of rayon fibers in a comprehensive way in order (a) to see whether new evidence with regard to the correct separation of "background" and crystalline interference could be obtained, and (b) to attempt comparative intensity measurements on some of the principal crystalline interferences. These were: 101, $10\bar{1}$, and 002 (A_0, A_2, and A_4 on the equator); 020 and 040 (on the meridian); and 021 (on the second layer line). To that end, several radial and azimuthal scans were taken as required. The former (see R in Figure 2) gave plots of intensity against 2θ at a preselected azimuth α; the latter (see A in Figure 2) plots of intensity against azimuth α at a preselected value of the diffraction angle 2θ.

The minimum number of scans made were: *Radial* over the centers of all selected interferences, thus on the equator ($\alpha = 0$), meridian ($\alpha = 90°$), and at the azimuth of the 021 line ($\alpha = 57.4°$). *Azimuthal* at the value of 2θ of all selected interferences. From the former the "line-width," $b(2\theta)$, of the interferences can be derived (which stands in relation to the size and perfectness of the crystallites). From the latter the azimuthal extension, $b(\alpha)$, can be derived (which stands in relation to the distribution of the orientation of the crystallites in the fiber).

In order to find a generally applicable measure for the *intensity* of an interference, some suitable integration procedure had to be accepted. However, first of all the most probable background line had to be agreed upon. The intensity of the interference in question was then taken as that of the "peak" on top of the background.

The background evaluation will be treated in Section 6. We shall here assume that a background line has been found.

The procedure selected is illustrated with the diagrammatic Figures 3 and 4. Figure 3A represents a radial scan over the locus of maximum intensity of the peak in question (f.i. $\alpha = 0$ for the equator peaks). The dotted line is the accepted background line. In Figure 3B the azimuthal scan of the same peak is represented. The surface S_R of the peak on the radial curve was determined in cm.^{2} and divided by its height in cm. (h in Figure 3A) in order to find $b(2\theta)_i = S_R/h$, representing the "integral halfwidth," $b(2\theta)_i$, of the peak.

Then, the surface S_A of the peak above the background in the azimuthal scan was measured in cm^2.

As a measure of total peak intensity was taken

$$I_{hkl} = S_A b(2\theta)_i$$

The value of I_{hkl} was then normalized according to Equation 1 in order to find $I_n(hkl)$.

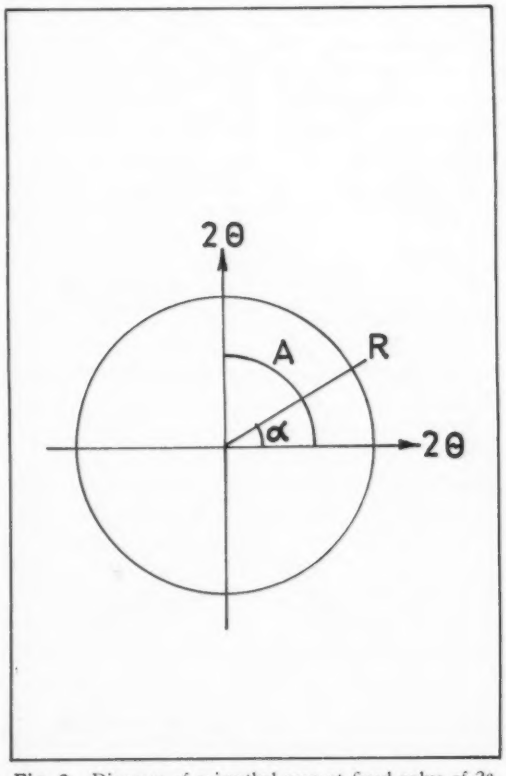

Fig. 2. Diagram of azimuthal scan at fixed value of 2θ and radial scan R at fixed value of azimuth α.

In the case of the interferences A_3 and A_4, which lie near to each other and do not become separated (see diagrammatic representation of the case in Figure 4), two procedures were tried. First a very simple approximation was attempted, taking

$$b(2\theta)_i = S/(h_3 + h_4) \tag{3}$$

using the experimental values of h_3 and h_4 as represented in Figure 4, and expressing the total intensity of $A_3 + A_4$ through

$$I_{A_3+A_4} = (S_{A_3} + S_{A_4}) \cdot b(2\theta)_i \tag{4}$$

Second a rather elaborate procedure was applied in order to find out the magnitude of the error which might be introduced by this application. Starting from the experimental values of h_3 and h_4 (as indicated in Figure 4), the experimental location 2θ of the two maxima and the surface of $A_3 + A_4$ on the equator recording, the assumption was introduced that the peaks can be represented by Gaussian functions and that A_3 and A_4 have equal radial integral halfwidths. By applying an iterative mathematical procedure worked out by Dr. B. G. Wiggers of Arnhem and explained in the Appendix, the true locations and heights of the maxima and the true halfwidth value were calculated.

Then two azimuthal scans were taken over the two observed maxima and the surfaces corresponding to A_3 and A_4 measured. The latter were corrected by multiplication with the ratio of the calculated and the experimental values of h_3 and h_4, respectively. The total intensities of A_3 and A_4 were again expressed as the product of the corrected azimuthal surface S_a and the calculated halfwidth.

It turned out that, owing to mutual compensation of the error in the surface and that in the halfwidth, the sum of the calculated surfaces was quite insignificantly different from that obtained by the approximation in Equation 4. The difference was 1% or less (cf. Appendix). Thus for intensity determinations only, the simple procedure can be applied.

The differences in the values of the halfwidth and peak location were of course larger. Still the former remained below 7% (cf. Appendix). As we are not primarily interested in these quantities in the present context, we shall quote below the figures obtained with the approximative method. We remark that, quite correctly, the intensities thus measured are not directly proportional to the fraction of the scattering crystalline material. Theoretically, the surfaces S_A should be corrected by multiplication of each ordinate, I, with the cosine of its azimuth in order to find the value $\int I \cos\alpha \, d\alpha$ which is proportional to that fraction (in lieu of $\int I_\alpha \, d\alpha$ as used in this paper). We have refrained from applying this correction because it does not significantly affect the results given in Table II.

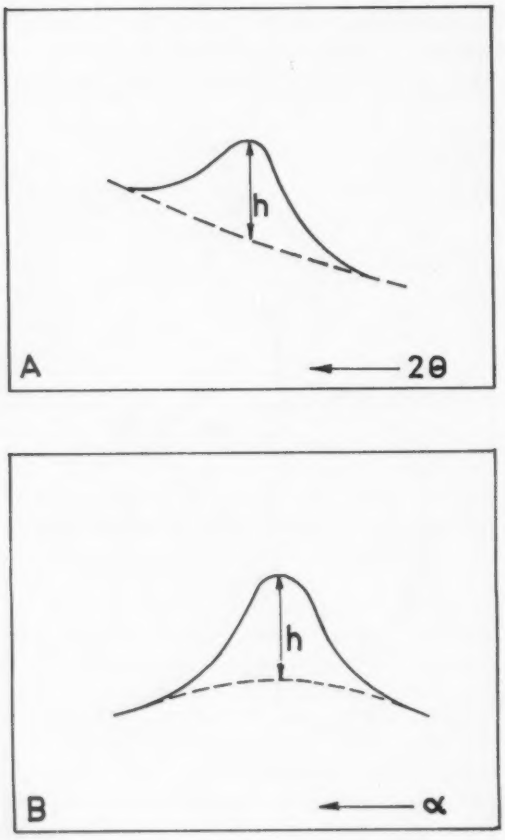

Fig. 3. Radial scan over intensity maximum of a crystalline interference (A) and azimuthal scan over same (B) (diagrammatic).

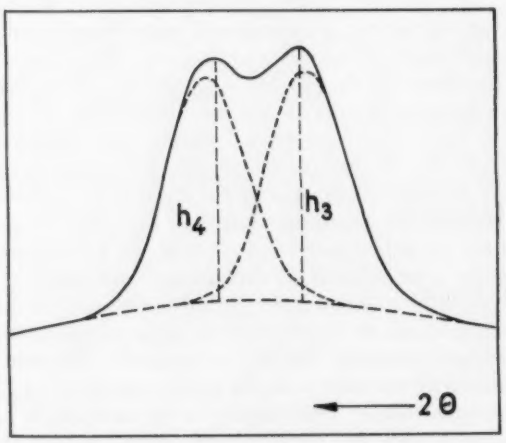

Fig. 4. Diagrammatic representation of the overlap and resolution of the A_3 and A_4 lines.

In this paper normalized total peak intensities will be designated by ${}_nI_{hkl}$.

Background intensities were, of course, also normalized using Equation 1. As will be discussed in Section 6, no attempt was made to find a general measure of background intensity comparable from specimen to specimen. The distribution of background intensity in oriented cellulose fibers turned out to be anisotropic and so complicated that no unambiguous means to express its "total intensity" in some integral figure was found.

This is in contrast to oriented nylon and polyethyleneterephthalate fibers, where it could be shown that the "amorphous background" is centrosymmetrically distributed with a maximum of intensity at a given angle of diffraction. In that case, this maximum value can be employed as a comparable measure of background intensity.

6. Evaluation of Background

It was our hope that monochromatic diffractometer recordings with their implicate high resolution and freedom from several disadvantages inherent in previously used X-ray techniques might give better information on the intensity distribution of the background. Actually, a thorough study of the recordings has led us to a background line different from that previously assumed. In the following we shall explain how this background line was arrived at. Though we are aware that this is still not a physically well founded procedure, it is felt that it is more unambiguous than any earlier attempt. It is based on close scrutiny of the entire spatial distribution of diffracted intensity.

This study has made it impossible to assume, as previously, that the background maximum would lie at the locus of the minimum between the A_0 and A_3 peaks (Figure 1). The maximum must rather lie somewhere under the center of the A_3A_4 peak. This is in line with an earlier investigation by the authors using a different technique [8c, 10].

As it is impractical to reproduce all the recordings used, even in the case of one specimen, we shall only treat some typical examples which may serve to explain how the background line was arrived at.

In Figures 5 and 6 are reproduced the radial recordings along the equator and the meridian of Specimen 704 and in Figure 7 the azimuthal recording over the center of A_3 ($2\theta = 20.2°$). It is seen that on the meridian it is relatively easy to deduce the background line without too much ambiguity. The background at $2\theta = 20.2°$ in Figure 6 must coincide with that at $\alpha = 90°$ in Figure 7, and is in both cases a point of the actual recording. There is no obvious reason to assume a contribution from crystalline interferences at this point.

In Figure 7 we have assumed that in this very highly oriented specimen the 021 and A_3 lines do not overlap. The background line (broken curve) is therefore drawn as a smooth curve passing through the point of recording on the meridian and the minima between 021 and A_3. In this way we find the probable height, h_0, of the background on the equator (at 0° in Figure 7). This point is then transferred to the equator recording (Figure 5). Other points of the background line in Figure 5 are obtained as follows. First we smoothly extrapolate the background at about 30° towards its position under A_3, and then we attempt to do the same starting from the background at low angles (about 5°). In this, we are guided by the fact that the beginning of the A_0 line can be well detected (at $2\theta = 7.5°$) as well as its maximum (at $2\theta = 12.1°$). Drawing the vertical through this maximum we can construct a mirror image of A_0 on the high-angle side of this vertical. The result demonstrates that at the locus of the minimum of the recording between A_0 and A_3 (at $2\theta = 12.1° + 2.4° = 14.5°$) there is still an intensity contribution by A_0 which is given by a symmetry consideration from the height of A_0 at $2\theta = 12.1° - 2.4° = 9.7°$.

If we can find evidence that the A_3 peak does not contribute to the minimum at 14.5°, then the contribution of the background at the minimum is given by subtracting the height of A_0 at 9.7° from the minimum (point indicated by arrow in the figure).

This evidence is found as follows. Verticals are drawn through the maxima A_3 and A_4. It is then seen that A_4 extends to 5.5° beyond its vertical towards the high-angle side. Making the not unreasonable assumption that the extension of A_3 towards the low-angle side is also 5.5° from its own vertical, which is at $2\theta = 20.2°$, we find that at the locus of the minimum the contribution of A_3 has just about become zero.

Connecting the background at very low angles with the point indicated by the arrow and the point already found under A_3 by a smooth curve, the background line is completed. It appears as a curve with a flat maximum under A_3 and A_4.

In Figures 8, 9, and 10 are reproduced the corresponding recordings of Specimen 705, in which the

(broken) background lines were constructed in a similar way.

It is important to notice that, owing to less orientation in this specimen, there is clearly a contribution of 021 on the meridian at 20.2° (Figure 9) as shown by a maximum appearing near the 020 peak at its high-angle side.

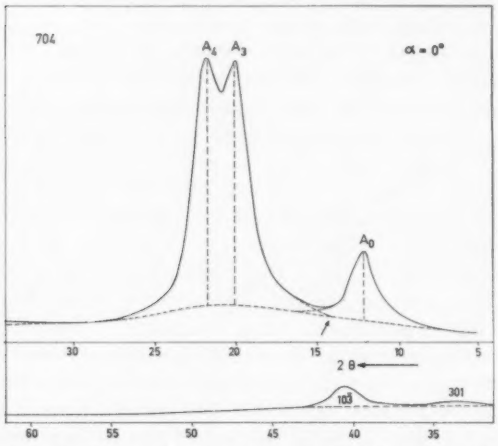

Fig. 5. Equatorial scan of Specimen 704 corrected for air scattering. Separation of the crystalline interferences from each other and from the background indicated by broken lines.

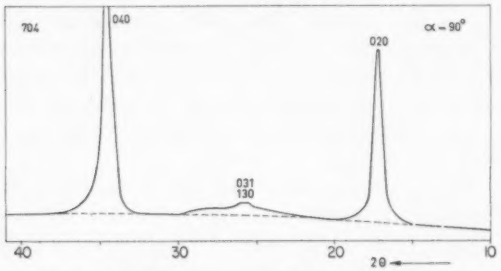

Fig. 6. Meridional scan of Specimen 704 corrected for air scattering.

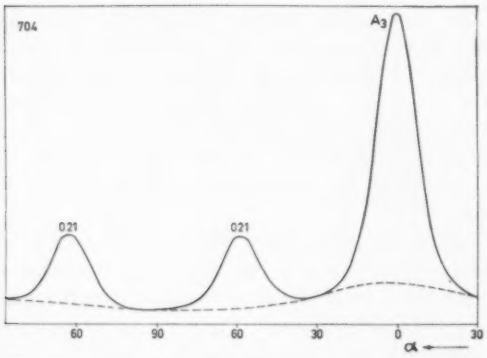

Fig. 7. Azimuthal scan over maximum of A_3 ($2\theta = 20.20°$) for Specimen 704 corrected for air scattering (at twice the intensity of Figure 6).

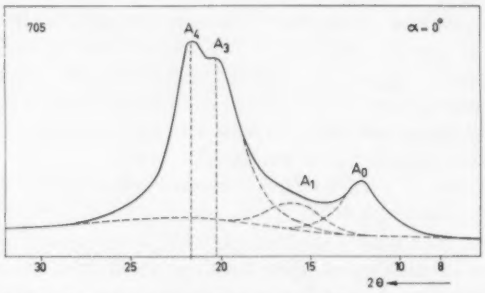

Fig. 8. Equatorial scan of Specimen 705 corrected for air scattering, showing the resolution of the A_1 peak.

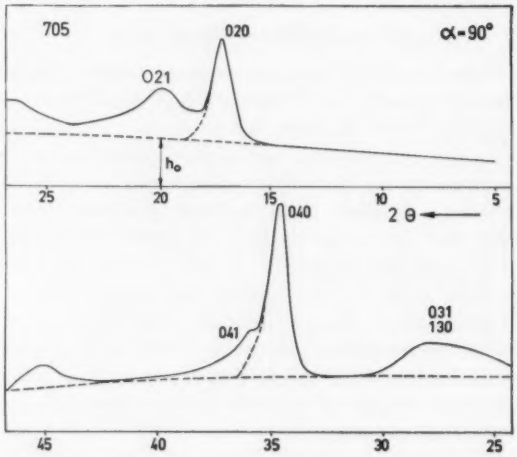

Fig. 9. Meridional scan of Specimen 705 corrected for air scattering; note the contribution of 021 on the meridian in contrast to Specimen 704 (Figure 6).

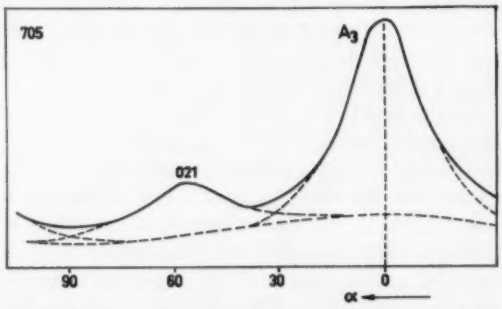

Fig. 10. Azimuthal scan of Specimen 705 over maximum of A_3 at $2\theta = 20.20°$ (cf. Figure 7) corrected for air scattering (at twice the intensity of Figure 9).

It is shown in Figure 10 how resolution of the overlapping 021 lines from each other and from A_3 was attempted. This construction gives a fairly good lead as to how smooth extrapolation of the background towards the center of the A_3 line should be performed in order to find the approximate height of the background under the A_3 maximum. Transfer of the latter to the equator recording (Figure 8) should fit the background constructed on the equator recording according to the indications given above for the case of Sample 704. By balancing the requirements of the equator recording (Figure 8) with those of the azimuthal recording (Figure 10), a background line satisfying both can be found without difficulty or undue ambiguity.

Operating in this way, it is found (see Figure 8) that the intensity recording between the maxima of A_0 and A_3 cannot be duly accounted for without accepting the occurrence of another line located between them. The maximum of this line is found to lie with fair approximation at the angle associated with the A_1 line of the cellulose IV modification.

Obvious evidence for a contribution from this cellulose IV line was only met with in Specimens 705, 706, and 707. Though it is felt that the procedure in question is not sure enough to allow other than rough deductions on the content of cellulose IV in a specimen (in particular small amounts of cellulose IV may escape attention), it seems rather certain that the occurrence of cellulose IV in rayons is more frequent than previously realized. Its formation seems to be intimately related to the temperature at which the decomposition of the xanthate gel or the dehydration of the primary gel takes place.

In Figure 11 is shown the equator recording of Specimen 706, which had the largest content of cellulose IV in the series.

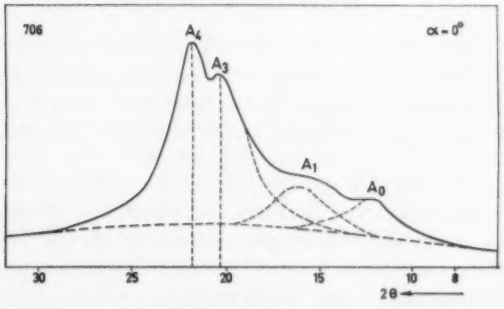

Fig. 11. Equatorial scan of Specimen 706 corrected for air scattering, showing the resolution of the A_1 peak.

It is seen that the occurrence of cellulose IV in 706 was already obvious from the presence of a flat maximum between A_0 and A_3 in the original recording. The construction of the background line and the resolution of the peaks were performed according to the principles previously described.

The construction always led to a maximum of the cellulose IV line very near to $2\theta = 15°$ (theory: 14.8°). Since in cellulose IV the A_3 peak is nonexistent and only the A_4 peak occurs, the intensity of A_4 should be enhanced relative to A_3 if a sample contains cellulose IV. It will be shown below that a qualitative correlation of this kind was actually found.

Finally, we reproduce in Figure 12 the equatorial scan of the mercerized Specimen 709. No indication of the occurrence of cellulose IV was found.

By meticulous investigation of a large number of additional radial and azimuthal recordings at suitably chosen angles, which can neither be discussed nor all reproduced here, we have attempted to study the distribution of the background intensity over the entire diagram. The result for 704 is given in Figure 13. Here the normalized background intensity along azimuthal recordings at various values of 2θ (compare insert in the top right corner of Figure 13) is plotted as a function of azimuth. It is seen that the maximum intensity on the equator lies at about $2\theta = 20°$ and the maximum intensity on the meridian at about $2\theta = 35°$. Both maxima, that on the equator

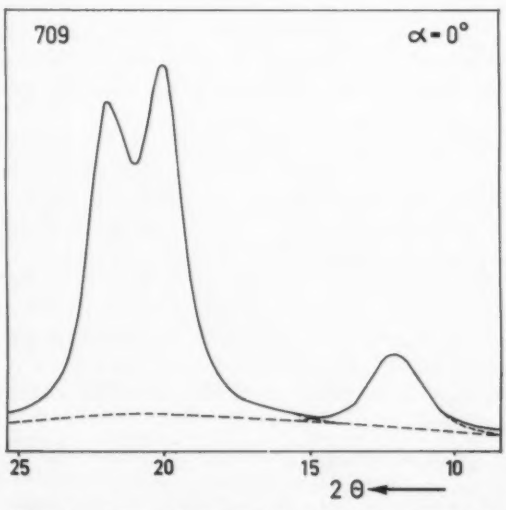

Fig. 12. Equatorial scan of the previously mercerized Specimen 709 corrected for air scattering.

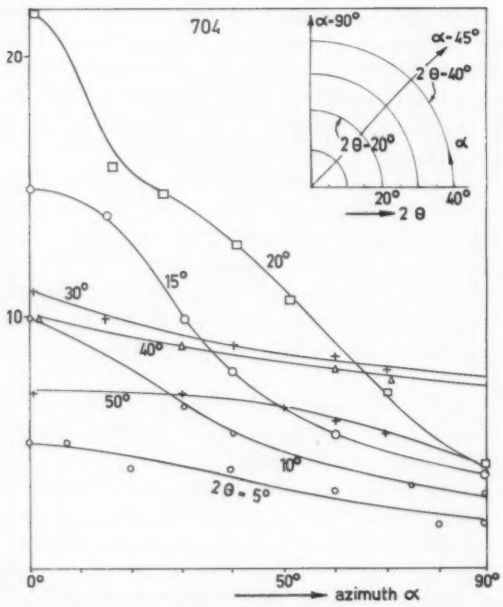

Fig. 13. Background intensity of Specimen 704 as a function of azimuth at various angles of diffraction 2θ corrected for air scattering.

and that on the meridian, seem to be located under the interferences with the largest intensity. (This may have something to do with the gradual transition between crystallites and "amorphous" regions.)

Hence, in the case of cellulose, there is no question of an essentially isotropic "amorphous" ring as present in the diagrams of oriented partially crystalline polyethylene, natural rubber, and nylons. The background is anisotropic in a complicated fashion. (An earlier contrary statement by the authors in Reference 11 has to be withdrawn.)

Owing to this involved intensity distribution we could not find a suitable means of expressing its intensity in a single quantity proportional to the total of "amorphous scatter." This cuts out the possibility of other than relative determinations of crystallinity.

The background lines arrived at here lie considerably lower than those previously assumed. It is believed that they are a better approximation, though we are aware that exact knowledge of the mathematical shape of the peaks would be required for a better judgment.

If the peaks conform to a Gauchy-type curve as suggested by Viervol et al. [2], our background lines may still lie too high. However, according to these authors, the intensity curves of rayon cannot be described as a superposition of Gauchy curves alone without leaving a diffuse background which is estimated to correspond with about 40% of the material [2a].

Now, what is the consequence of the foregoing with regard to the previously proposed quantitative procedures for measuring orientation and crystallinity?

The determinations of orientation will be little affected, since they are only concerned with the relative change of the height of the peaks as a function of azimuth, which is hardly, if at all, affected by drawing the background line in the old manner (also see Section 9).

How the outcome of the old procedure for crystallinity determination is affected by the present results cannot be predicted as it did not depend on the proportion of the scattering of the crystalline and amorphous portions in one given sample, but on the relative intensities of the crystalline and the amorphous scattering, respectively, in a series of samples.

The present authors wish to remark that, in contrast to what has been imputed to them by others on several occasions [7a], they never claimed exactness or strict physical significance with regard to the outcome of these determinations [7b]. The method was introduced for prospecting at a time when there existed no information whatsoever on the degree of crystallinity of cellulose and most other polymers. In allowing differentiation between various cellulose specimens and in giving at least some quantitative idea of the crystalline fraction, it has fulfilled a useful purpose in cellulose research. Moreover, the correct order of magnitude of the results has been corroborated by later infrared measurements [19].

It will be shown below that the relative values of the crystallinity arrived at by the present method are of the same magnitude as those indicated by the old method.

7. Evaluation of the Intensity of the Crystalline Interferences

The procedure followed is that already described in Section 4. In Table I are listed the values of the normalized intensities, I_n, and in Table II those of the integral halfwidths, $b(2\theta)_i$, of the principal interferences.

It is seen that, according to the observed intensities of the majority of the lines, the sequence of increasing crystallinity of the specimen is 706, 705, 707, 704, 709. Only the 021 line shows quite anomalous proportions, and in the case of the cuprammonium rayon (707) the two meridional lines are abnormally weak.

TABLE I. Values of I_n (*hkl*) from Observations

hkl		2θ	704 fiber G	705 text. rayon	706 cord rayon 083	707 cupr. rayon	709 mercer. fiber G
Paratropic							
101	(A_0)	12.1°	0.375	0.42	0.21	0.41	0.47
10$\bar{1}$	(A_1)	14.0°	—	0.21	0.255	0.095	—
10$\bar{1}$	(A_2)	20.2°	1.29	0.97	0.715	1.23	1.59
200	(A_4)	21.4°	1.30	1.09	0.775	1.23	1.34
Diatropic							
020		17°	0.163	0.078	0.054	0.103	0.186
040		34.8°	0.242	0.185	0.136	0.146	0.246
2nd layer line							
021		20.2°	0.214	0.41	0.255	0.35	0.260
Sum			3.59	3.37	2.40	3.56	4.09

TABLE IA. Intensity Ratios of Some *hkl* Reflections Calculated from Table I

	704	705	706	707	709
A_0/A_2	0.29	0.43	0.30	0.34	0.29
$021/A_2$	0.16	0.42	0.36	0.28	0.16
$020/A_2$	0.13	0.08	0.075	0.085	0.12
$040/A_2$	0.19	0.19	0.19	0.12	0.16
A_2/A_4	0.99	0.89	0.92	1.00	1.18

TABLE II. Crystalline Fraction as Derived from the Present Measurements if that of 705 is Set Equal to 0.40 Compared with the Results Obtained by the Method of References 7 and 11

	Specimen No.				
	704	705	706	707	709
From sum of all lines listed in Table I	0.425	(0.40)	0.285	0.42	0.485
From $A_0+A_1+A_2+A_4$ only	0.446	(0.40)	0.28	0.440	0.50
Old value	0.48	0.40	—*	0.40	0.52

* Indeterminable owing to high content of cellulose IV.

If it were assured that any one *hkl* reflection represents a given constant fraction of the total intensity diffracted by the crystalline portion, then the intensity of any chosen *hkl* line in the five specimens could serve as a relative measure of crystallinity. This would also be so for the sum of the intensities of several *hkl* reflections, which would—because of compensation of experimental errors—give a more accurate measure.

Unfortunately the experimental data given in Table I reveal that this simple procedure, which requires that the various *hkl* reflections in a given specimen stand in constant proportion to each other, seems not to be justified. Some of these proportions are given in Table IA.

It is seen that approximately constant proportions are found only between the meridional lines and A_2, while in the other cases considerable variations occur.

The variability of the proportion A_2/A_4 in rayons has long been known. According to Andress' calculations from his model of the cellulose II lattice [1] it should be 1.33. Table IA demonstrates that only in cuprammonium rayon (707) and in the mercerized specimen (709) is the ratio larger than 1, but even in the latter it remains below the theoretical value.

The predominance of A_4 in 705 and 706 can readily be associated with the obvious presence of cellulose IV in these specimens (Figures 8 and 11), since in the spectrum of this modification the A_2 line does not occur.

In view of the variable proportion between the lines as demonstrated in Table IA, a difficulty arises in devising an unambiguous procedure to derive a relative measure of crystallinity from the data listed in Table I. The most desirable way seems to be to measure the sum of the intensities of all interferences, including those not listed in Table I. Unfortunately this is practically impossible.

However, as shown in Table II, one arrives at rather consistent figures if either the sum of all measured lines or the sum of the equatorial lines is taken as a relative measure of crystallinity. In order to facilitate comparison with crystallinity determinations by the old method [7, 11] the crystalline fraction of 705 has been arbitrarily set equal to 0.40,

which is the figure found by the old method. (The results of the old method are given in the third line of the table.)

It is seen that the earlier results are not very far out of line as compared to the present ones, despite the different construction of the background line in the two cases.

The present method does not provide means of estimating absolute values of crystallinity as we could not find an unambiguous method of evaluating the over-all background intensity over the whole quadrant.

At the present moment we believe that there is very little hope that more or better information can be expected from X-ray techniques.

In order to make a comparison with the cellulose II intensities following from Andress' model, Table III is given. As only relative values are concerned, we have set the sum of the A_3 and A_4 lines equal to 100 in all cases.

Since Andress has calculated the intensities for the case of the Debye-Scherrer method of exposure accounting for the Lorentz factor and for polarization after the equation

$$(1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$$

the figures taken from his table were multiplied by the factor

$$\frac{\sin^2\theta \cos\theta}{1 + \cos^2 2\theta} \cdot \frac{1 + 0.79 \cos^2 2\theta}{\sin 2\theta}$$

in order to account for the fact that in our case the "rotating crystal method" is concerned where the factor

$$(1 + 0.79 \cos^2 2\theta)/\sin 2\theta$$

obtains for the Lorentz and polarization factors. (0.79 is the $\cos^2$ of the reflection angle at quartz monochromator employed.)

It is seen that, roughly, the conformity is fair, although significant deviations occur and the scattering between the rayon specimens is also significant. The most salient feature is perhaps the ratio between the meridional 040 and 020 intensities, which is about 4 according to Andress and nearer to 1 in specimens 704, 707 and 709. The higher value of about 2 in 705 and 706 can perhaps be related to a content of cellulose IV. The lattice of cellulose IV is nearly akin to that of cellulose I, and according to Meyer and Misch the ratio in question is about 6 in cellulose I. Our own measurements on ramie [14], however, even gave 12. Another feature is the much lower experimental figure for A_7 and III_1 lines.

To our knowledge, this is the first time that the relative intensities of cellulose II lines have been measured and not merely visually estimated.

More lines than those referred to above were observed but not measured owing to doubtful accuracy due to overlap. II_2 (122) and II_4 ($12\bar{2} + 22\bar{1}$), both listed by Andress with a slightly higher intensity than 020, were clearly present; III_4 ($13\bar{2} + 23\bar{1}$) and IV_2 ($14\bar{1} + 241$) were detectable. Of A_5 (301) and A_6 (303), both having negligible intensity according to Andress, the former was detectable, the latter not.

8. Evaluation of Line Width

In Table IV the observed integral line widths are collected and listed in the sequence of decreasing line width of the A_3 and A_4 lines. It is seen that the tire cord rayon shows the widest equatorial lines. Much

TABLE III. Comparison of the Observed Relative Line Intensities with Those Calculated for the Andress Model ($A_3 + A_4$ set Equal to 100)

Andress' symbol:	A_0	A_3A_4	II_0	IV_0	II_1	A_7	III_1	IV_1
Miller indices:	101	$10\bar{1}$	020	040	021	$20\bar{2}$	031	041
		002				$10\bar{3}$	131	
							130	
2θ, degrees:	12.2	20.2	17.2	34.4	20.1	40.7	28.5	36.5
		21.7						
α, degrees:	0	0	90	90	57.4	0	66.9	72.5
							57.3	
							64.4	
704	14.5	100	6.3	9.4	8.3		(not measured)	
705	20.5	100	3.8	9.0	19.6		(not measured)	
706	14.2	100	3.6	9.1	17.0		(not measured)	
707	16.8	100	4.2	5.9	14.1		(not measured)	
709	16.2	100	6.4	8.6	8.9	3.1	6.1	4.2
Andress	10.4	100	3.9	15.7	12.8	17.1	20.5	2.7

TABLE IV. Integral Line Widths, $b(2\theta)_i$, in Degrees

hkl		706 cord rayon	705 text. rayon	707 cupr. rayon	704 fiber G	709 mercer. fiber G
(101)	A_0	3.45	3.20	2.58	2.36	2.56
101	A_3	2.66	2.35	2.13	1.96	1.82
002	A_4					
020	II_0	1.05	1.17	1.13	0.72	0.68
040	IV_0	1.25	1.31	1.05	0.83	0.82

evidence is in favor of the view that in tire cord rayons (of the so-called "all skin" type) the average crystallite size is smaller than in the ordinary rayons while their crystallinity is but slightly lower. This view, first expressed by Morehead and Sisson in 1953 [20] is corroborated by Table IV with regard to the lateral dimensions. In the case of the longitudinal dimensions the difference is insignificant. This would indicate that in tire cord rayons the crystallites are thinner than in textile rayon while they have about the same length. As is well known, however, line widths are associated with crystallite dimensions as well as with lattice perfection.

In Table V the crystallite dimensions following from Table IV are calculated by applying Scherrer's simple relation

$$h = 0.89\lambda/b \cos \theta$$

in order to find the order of magnitude of the crystallites, neglecting the effect of lattice imperfections. These figures will then represent the lower limit of the crystallite dimensions.

Comparing 704 and 709, it is seen that, practically, mercerization does not change the particle size though the crystallinity increases (Table I).

9. Evaluation of Orientation

Orientation is associated with the azimuthal intensity distribution. According to References 5, 6, 8 we have the relationships

$$f_x = 1 - \tfrac{3}{2}\,\overline{\sin^2\gamma} \quad \text{or} \quad f_x = 1 - \tfrac{3}{2}\,(\overline{\sin^2\alpha} + \overline{\sin^2\beta})$$

where f_x is the orientation factor of the crystallites, $\sin^2\gamma$ the average square sine of the azimuthal spread of the intensity on a diatropic interference (either 020 or 040) and $\overline{\sin^2\alpha}$ and $\overline{\sin^2\beta}$ are those of the A_0 and A_3 interferences, respectively.

In the classical method, where photographic exposures on a flat film are employed, the second formula referring to the two paratropic lines is always applied since the diatropic lines are much weaker and do not correctly appear on flat film. The diffractometer recordings allow the using of both equations independently, which then should yield consistent results.

TABLE V. Lower Limit of Particle Size in Angstroms Calculated from Table IV Using Scherrer's Equation

		706	705	707	704	709
⊥axis	101 (A_0)	23	25	31	34	31
	A_3–A_4	30	34	38	41	44
∥axis	020	76	68	71	111	118
	040	66	59	79	100	101

We have carried out the entire procedure for Specimen 704 and the results are collected below.

$\overline{\sin^2\alpha}$ (from A_0) 0.025; $\overline{\sin^2\beta}$ (from A_3) 0.0215 $f_x = 0.926$
$\overline{\sin^2\gamma}$ (from 020) 0.0388 $f_x = 0.942$
$\overline{\sin^2\gamma}$ (from 040) 0.0362 $f_x = 0.946$

It is seen that the orientation factor derived from the paratropic lines conforms with that derived from both diatropic lines which confirms the theory given in Reference 5.

10. Location of the A_3 and A_4 Lines

Taking the measured location of the A_4 maximum as corresponding to 4.07 ± 0.03 Å, the lattice spacings corresponding to the calculated correct locations of A_3 and A_4 for the six rayon specimens are averaged:

A_3 4.35 ± 0.03 A_4 4.09 ± 0.01

This is very little (no more than 2%) different from all earlier accepted values.

Acknowledgment

The X-ray experiments were carried out by one of us (W) in the Physical Laboratory of the Technical University in Delft. The authors are indebted to Professor P. M. de Wolff for frequent technical guidance.

Literature Cited

1. Andress, R. K., *Z. physik Chem.* **B4**, 190 (1929); cf. Ref. 18, p. 166.
2. Gjönnes, J., Norman, N., and Viervol, H., *Acta Chem. Scand.* **12**, (a) 489, (b) 2028 (1958).
3. Goppel, J. M. and Arlman, J. J., *Appl. Sci. Research* **A1**, 3, 18, 347 462 (1947); **A2**, 1 (1948).
4. Heikens, D., Hermans, P. H., and Weidinger, A., *J. Polymer Sci.* **35**, 139, 145 (1959).
5. Hermans, J. J., Hermans, P. H., Vermaas, D., and Weidinger, A., *Rec. trav. chim.* **65**, 437 (1946).

6. Hermans, P. H., "Contribution to the Physics of Cellulose Fibers," Amsterdam-New York, Elsevier. 1946, p. 158.
7. Hermans, P. H., *Kolloid Z.* **120**, (a) 3, (b) 23 (1951).
8. Hermans, P. H., "Physics and Chemistry of Cellulose Fibers," Amsterdam-New York, Elsevier. 1949, (a) p. 229; (b) p. 517; (c) 262.
9. Hermans, P. H. and Weidinger, A. See Reference 14.
10. Hermans, P. H. and Weidinger, A., *Rec. trav. chim* **65**, 620 (1946).
11. Hermans, P. H. and Weidinger, A., *J. Appl. Phys.* **19**, 491 (1948); *J. Polymer. Sci.* **4**, 135 (1949).
12. Hermans, P. H. and Weidinger, A., *J. Polymer Sci.* 4, 709 (1949).
13. Hermans, P. H. and Weidinger, A., *Makromol. Chem.* **39**, 67 (1960).
14. Hermans, P. H. and Weidinger, A., TEXTILE RESEARCH **31**, 571 (1961).
15. Klug, H. P. and Alexander, G. E., "X-ray Diffraction Procedures," New York, Wiley, 1954. p. 281.
16. Kratky, O. et al., *Kolloid Z.* **64**, 213 (1933); **86**, 245 (1939); **96**, 30 (1941).
17. Krimm, S. and Tobolsky, A. V., *J. Polymer. Sci.* **7**, 57 (1951).
18. Mark, H., "Physik und Chemie der Cellulose," Berlin, Springer, 1932. Andress, R. K., *Z. physik. Chem.* **B4**, 190 (1929).
19. Marrinan, H. J. and Mann, J., *J. Polymer Sci.* **21**, 301 (1956).
20. Sisson, W. A. and Morehead, F., TEXTILE RESEARCH JOURNAL **23**, 152 (1953).
21. Wakelin, J. H., Virgin, H. S., and Crystal, E., *J. Appl. Phys.* **30**, 1654 (1959).
22. Wolff, P. M. de, Lowitzch, K., and Parrisch, W., "Abstr. of Symposium Intern. Union of Crystallography," Madrid, 1956, p. 25. Wolff, P. M. de, *Acta Cryst.* **13**, 835 (1960).
23. Wuorinen, O. A., *Paperi ja Puu (Paper and Timber)* **37**, 335 (1955); **38**, 479 (1956).

Manuscript received October 10, 1960.

Appendix

The problem (see Figure 14) consists of finding the true heights η_1 and η_2 and the true locations μ_1 and μ_2 of the maxima of two superimposed Gaussian curves 1 and 2 (fully drawn), if the heights h_1 and h_2 and the distance d of the two maxima in the composite curve (broken curve) are given, under the assumption that the half-width b of the two component curves is equal and given by $b = S/\eta$ (S = area under the curve).

If y is the ordinate of the Gaussian curve, then

$$y = \frac{S}{\sigma\sqrt{2\pi}} \exp[-(x-\mu)^2/2\sigma^2] \qquad (1a)$$

It can be easily derived that

$$b = \sigma\sqrt{2\pi} \qquad (2a)$$

$$y = \eta \exp[-(x-\mu)^2/2\sigma^2] \qquad (3a)$$

The ordinate of the composite curve and its given surface S_R are expressed by

$$y = y_1 + y_2 = \eta_1 \exp[-(x-\mu_1)^2/2\sigma^2] + \eta_2 \exp[-(x-\mu_2)^2/2\sigma^2] \qquad (4a)$$

where y_1 and y_2 are the ordinates of the component curves.

$$S_R = S_1 + S_2 = (\eta_1 + \eta_2)\sigma\sqrt{2\pi} \qquad (5a)$$

The values of h_1 and h_2 follow from Equation 4a by substitution of x by x_1 and x_2 respectively, where x_1 and x_2 are the observed abscissa values of the composite curve. If we arbitrarily set $x_1 = 0$, then $x_2 = d$. Thus we get

$$h_1 = \eta_1 \exp[-\mu_1^2/2\sigma^2] + \eta_2 \exp[-\mu_2^2/2\sigma^2] \qquad (6a)$$

$$h_2 = \eta_1 \exp[-(d-\mu_1)^2/2\sigma^2] + \eta_2 \exp[-(d-\mu_2)^2/2\sigma^2] \qquad (7a)$$

Since differentiation of Equation 4a with respect to x gives an expression equal to zero, for $x = x_1 = 0$ and $x = x_2 = d$ we find

$$\mu_1\eta_1 \exp[-\mu_1^2/2\sigma^2] + \mu_2\eta_2 \exp[-\mu_2^2/2\sigma^2] = 0 \qquad (8a)$$

$$(d-\mu_1)\eta_1 \exp[-(d-\mu_1)^2/2\sigma^2] + (d-\mu_2)\eta_2 \exp[-(d-\mu_2)^2/2\sigma^2] \qquad (9a)$$

From Equations 6a to 9a follows

$$\eta_1 = \frac{\mu_2 h_1}{\mu_2 - \mu_1} \exp[\mu_1^2/2\sigma^2] \qquad (10a)$$

$$\eta_2 = \frac{-\mu_1 h_1}{\mu_2 - \mu_1} \exp[\mu_2^2/2\sigma^2] \qquad (11a)$$

Eliminating η_1 and η_2 from Equations 5a, 6a, 7a, and 9a, three independent equations containing the unknowns σ, μ_1 and μ_2 remain. These three equations were solved numerically by an iterative method of which we shall omit the details here.

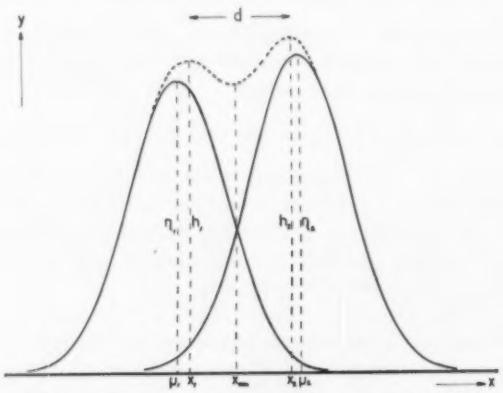

Fig. 14. Illustration of the resolution of the A_3 and A_4 lines by calculation (see text).

To exemplify the results of the calculation, the experimental data used and the results of the computation are collected below for Specimens 704 and 705.

	Experimental data used						Calculated	
	d, deg.	h_1, cm.	h_2, cm.	S_R, cm.^{2}	h_{min}, cm.	x_{min}, deg.	h_{min}, cm.	x_{min}, deg.
704	1.6	19.8	20.5	78.5	16.85	0.75	18.6	0.74
709	1.85	14.75	12.75	50.0	9.65	1.0	10.9	1.05

h_{min} and x_{min} refer to the height and location of the minimum between the A_3 and A_4 peaks.

The calculated values of η_1, η_2, μ_1, μ_2, and b were

	η_1	η_2	μ_1	μ_2	b	$\frac{S_R}{(h_3 + h_4)}$
704	18.31	18.91	−0.20	1.77	2.10	1.96
709	14.35	12.23	−0.06	1.94	1.89	1.82

In the last column the value of $S_R/(h_3 + h_4)$ is given (cf. Equation 3 in Section 5) for comparison with the correct value b following from the calculations.

Finally we give the sum of the total intensities of A_3 plus A_4 as derived according to Section 2 from b in combination with the observed azimuthal surfaces S_{A_3} and S_{A_4} corrected by multiplication with η_1/h_1 and η_2/h_2 respectively, along with the corresponding uncorrected values from the approximating Equations 3 and 4 in Section 5.

${}_nI_{A_3+A_4}$	704	709
Corrected	2.59	2.93
Uncorrected	2.58	2.90

As pointed out in Section 5, the difference is very small because of compensation of errors.

The authors are greatly indebted to Dr. B. G. Wiggers, Arnhem, for devising the method of the peak separation and for carrying out the calculations.

Literature

Buckingham, R. A., "Numerical Methods," London, Pitman Sons Ltd, 1957, pp 250–253, pp. 262–264.

Scarborough, J. B., "Numerical Mathematical Analysis," London, The Johns Hopkins Press, 1950, Geoffrey Cumberledge Oxford University Press, 1950, pp. 192–198.

Quantitative Evaluation of the X-Ray Diffraction of Ramie Fiber

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Institute for Cellulose Research of the AKU and Affiliated Companies, Utrecht, Holland [1]

Abstract

A quantitative evaluation of the principal paratropic and diatropic interferences of ramie fiber is undertaken using a diffractometer technique with Geiger counter detection and strictly monochromatized radiation. The relative intensities of the main crystalline interferences have been measured and found to be in reasonable agreement with those calculated for the Andress lattice structure. Absolute values of the crystalline fraction however could not be derived from the present results.

In addition to the preceding paper [1] concerned with rayon, a similar investigation has been carried out with a sample of native ramie fibers.

In Figure 1 the equatorial scan and in Figure 2 the meridonal scan of the ramie specimen are reproduced. The probable background as arrived at by interpolation is indicated by a broken line.

The evaluation of the normalized intensities and integral halfwidths of a number of crystalline peaks was performed as before. The results are presented in Table I. (No attempt was made to separate A_1 and A_2.)

It is seen that the halfwidth values are considerably smaller than those in the rayons. The lower limit of the "particle size" calculated from (002) and from the diatropic lines comes to 50 and 110 Å respectively.

If we add up the normalized intensities of all

[1] Communication No. 111.

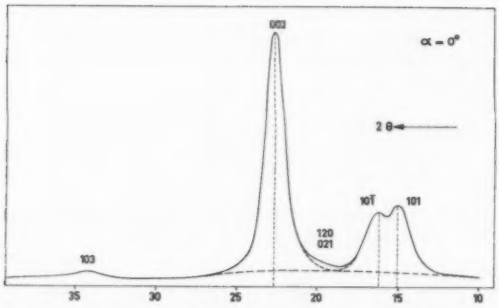

Fig. 1. Equatorial scan (corrected for air scattering).

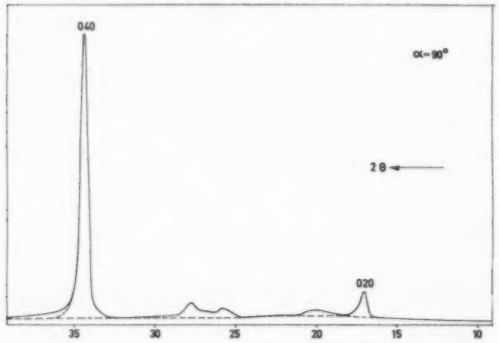

Fig. 2. Meridional scan (corrected for air scattering) taken at twice the sensitivity of that applying to Figure 1.

measured lines in Specimen 709 (mercerized Fiber G) of the preceding paper, each multiplied by the factor $\sin 2\theta/(1 + 0.79 \cos^2 2\theta)$ in order to account for Lorentz factor and polarization, we arrive at 1.02. For ramie the corresponding figure is 1.29.

Since the two figures approximate the total intensity scattered by the crystalline fractions, this would mean that the crystallinity of ramie is 1.26 times that of Specimen 709.

In Table II are compared the relative values of the measured intensities of the ramie lines with those calculated by Meyer and Misch [3].

The factor used by Meyer and Misch to account for Lorentz factor and polarization was practically the same as that applying in our case.

Except for the very much higher experimental intensity of the (040) line, the agreement is satisfactory.

TABLE I. Normalized Intensities I_n and Integral Half-widths $b(2\theta)_i$, in Degrees, of the Principal Ramie Lines

Andress symbol	Miller index	I_n	$b(2\theta)_i$
A_1	101	1.49	1.71
A_2	10$\bar{1}$		
A_4	002	2.65	1.57
A_{10}	004	0.16	1.56
II_0	020	0.06	0.71
IV_0	040	0.73	0.72
II_1	021	0.28	1.17
	120		
III_3	230	0.063	1.47
	032		
IV_2	042	0.118	1.17

TABLE II. Comparison of the Experimental Relative Intensities with Those Calculated from the Model of Meyer and Misch. The Value of the A_4-line Set Equal to 100

		Meyer and Misch	Experimental
A_1A_2	101 + 10$\bar{1}$	45	56
A_4	002	100	100
A_{10}	004	3.2	5.9
II_0	020	~1	2.3
IV_0	040	4.1	27.0
II_1	021 + 120	14.6	10.6
III_3	230 + 032	3.3	2.4
IV_2	042	—	4.5

In 1939 H. Kiessig [2] had already remarked that in native cellulose the 040 line is very much more intense than indicated by Meyer and Misch, if in flat film exposures the precaution is taken to set the fiber at an appropriate angle to the X-ray beam.

The weak "forbidden" line (030) discussed by previous authors was also (very weakly) observed in our recordings.

The X-ray experiments were carried out in the Physical Laboratory of the Technical University, Delft.

Literature Cited

1. Hermans, P. H. and Weidinger, A., TEXTILE RESEARCH JOURNAL **31**, 558 (1961).
2. Kiessig, H., *Z. physik. Chem.* **B43**, 79 (1939).
3. Meyer, K. H. and Misch, L., *Helv. Chim. Acta* **20**, 232 (1937).

Manuscript received October 10, 1960.

Letters to the Editor

Hygroscopicity of Acetylated Jute

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September 14, 1960

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

It has been shown in a previous communication [4] that the acetylation of jute has a marked influence on the intensity and spacing of the reflections A_x and A_y, and up to a certain stage of substitution the effect is very similar to that due to absorption of moisture [5]. Since under certain conditions of acetylation cellulose exhibits an enhanced hygroscopicity [2], it would be of interest to confirm that the observed effect is not due to a higher moisture content of the acetylated jute. The published results [2, 3] in this regard indicate that the regain of an esterified sample of cellulose is the sum of two components, one due to the unsubstituted hydroxyl groups and the other due to the acetyl groups, the acetyl group having a lower affinity for water than the hydroxyl group. The regain is thus determined by the degree of substitution, the proportion of the unsubstituted hydroxyls which remain accessible in a partial ester, and the extent of crystallization in a triester [3]. The relation between the degree of substitution and the regain also depends upon the method of preparation of the ester; it is linear up to complete substitution for heterogeneous reaction, the regain decreasing with the increasing degree of substitution [8], whereas for homogeneous reaction the regain increases at low degrees of substitution, reaches a maximum, and then falls off at high degrees of substitution [2]. This difference in the moisture affinity corresponding to the two methods of esterification is explained as due to the difference in the proportion of the accessible hydroxyl groups [2, 3]. In the heterogeneous method, substitution occurs more rapidly in regions immediately accessible to the reactants, and the originally inaccessible regions are only slightly affected in the early stages; while

TABLE I. Moisture Adsorption by Acetylated Jute and Cotton Fibers

Description of material	Acetyl content*	% Regain			
		18% RH	60% RH	66% RH	82% RH
Cotton, acetylated in	0 (native)	3.11	6.73	6.97	9.41
90–95 parts of ACOH	5.8	2.53	5.93	6.34	8.58
+ 5–10 parts of AC_2O.	19.8	1.42	4.09	4.61	6.27
Catalyst, $HClO_4$	53.8	0.75	3.16	3.93	5.41
	77.0	0.86	3.39	3.87	5.18
Jute, acetylated in 85	4.7 (native)	4.22	10.42	11.40	15.34
parts of ACOH + 15	8.0	3.62	9.11	10.06	13.65
parts of AC_2O.	28.4	1.51	4.96	5.71	7.79
Catalyst, $HClO_4$	51.1	1.03	3.88	4.50	6.10
	69.5	0.97	3.69	4.36	5.88
Jute, actylated in 50	4.7 (native)	4.22	10.42	11.40	15.34
parts of Xylene + 50	7.4	3.54	8.89	9.75	13.19
parts of AC_2O.	10.5	2.98	8.06	8.80	11.88
Catalyst, Sulfanilic acid	13.9	2.21	6.34	6.96	9.36
	17.8	1.65	5.01	5.62	7.60

* Acetyl content $= \frac{\text{Wt. of acetyl groups } (CH_3CO)}{\text{Wt. of dry fiber}} \times 100.$

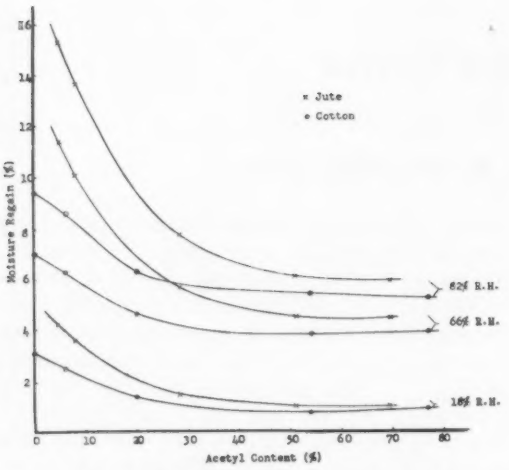

Fig. 1. Variation of moisture regain of acetylated jute and cotton (in glacial acetic acid medium) with acetyl content.

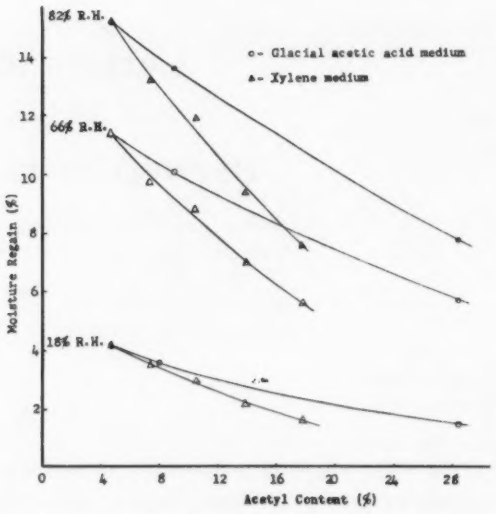

Fig. 2. Comparison of moisture regain of jute acetylated in glacial acetic acid medium with that in xylene medium.

the reaction continues by a process of opening up inaccessible regions, the freed hydroxyl groups are almost simultaneously substituted. On the other hand, in the homogeneous method, the more frequent introduction of the acetyl group on a cellulose hydroxyl prevents a number of adjacent hydroxyl groups from forming hydrogen bonds, and this increase in the number of available hydroxyl groups results in the increase in moisture regain at low DS. As the DS increases the number of hydroxyl groups freed by each substituted group decreases so that the moisture regain reaches a maximum and then decreases. Although the homogeneous method of acetylation was not employed in this investigation, in view of certain peculiarities of jute structure, e.g., higher amorphousness [6], more open structure [7], etc., one is not entitled to assume *a priori* that the reaction would proceed as in pure cellulose so far as the accessibility of the reactive groups is concerned. The present note aims at describing some results on the hygroscopicity of the progressively acetylated jute previously examined by X-rays [4].

The moisture regain was determined by the usual method of exposing the samples in weighing bottles to dry (over P_2O_5) and humid (over H_2SO_4 Soln.) atmospheres in a desiccator kept at $78 \pm 2°$ F. The samples were (i) jute and cotton fibers acetylated in glacial acetic acid medium, using acetic anhydride as the acetylating agent and perchloric acid as a catalyst [4] and (ii) jute alone acetylated at low degrees of substitution in xylene medium with sulfanilic acid catalyst. The immediate reason for including the latter is that the changes in the reflections A_x and A_y could also be followed in the corresponding X-ray photographs. The results are shown in Table I and Figures 1–3. The method of expressing the acetyl content as [Wt. of acetyl groups (CH_3CO—) × 100]/[Wt. of dry fiber] is retained in Table I and Figures 1–2, in pursuance of the previous convention [4]. But in order to facilitate a direct comparison with the published data [2] the same results are also presented in Figure 3, expressing the hygroscopicity in terms of molecules of water per polymer unit and the extent of acetylation as degree of substitution. We are aware that in view of the non-cellulosic inclusions of indefinite molecular weight, this system of calculation does not strictly apply in the case of jute. But it is also difficult to choose any other base than the anhydroglucose unit for this purpose. As for example, in view of the observations [1] that lignin *in situ* is acetylated more readily than cellulose and that an assessment of the rate of acetylation of the hemicelluloses *in situ* is not possible, the question of basing the calculation on the weighted mean of the three major constituents of jute cannot arise.

It is seen from Figure 1 that, expressed as percentage regain, the hygroscopicity of both cotton and

jute acetates decreases with increasing acetyl content up to almost complete substitution, but the decrease is not rectilinear as has been reported for heterogeneous substitution. On the other hand, when expressed as molecules of water per polymer unit (Figure 3) the hygroscopicity at first decreases, tends to reach a minimum at some intermediate stage, and then increases at higher degrees of substitution. This latter feature is more pronounced in cotton, and it is noted that the cotton sample is in a different physical state, practically losing the fiber structure at the last two stages of acetylation. Now, while the first phase of absorption can be taken to indicate that up to a certain stage of reaction the substitution occurs, as envisaged for the heterogeneous reaction, from the immediately accessible regions, and that the originally inaccessible regions are not sufficiently affected, the increase in the number of the available hydroxyl groups in the second phase seems to take place more rapidly than the rate of substitution, that is, more or less as has been suggested for the earlier stages of homogeneous reaction. Such a situation regarding the availability of the hydrophilic groups, as distinct from either of those corresponding to the two broad methods of esterification, might have arisen from factors connected with the details of the reaction, e.g., acetylating medium, catalyst, temperature of reaction, etc. A comparison of the results obtained by following two different procedures, one using xylene medium and sulfanilic acid catalyst and the other glacial acetic acid medium and perchloric acid catalyst (Figures 1 and 2) also points to a similar possibility, conceding that the difference is not due to any variation in the respective loss of weight. However, for both the procedures it is clearly seen that since at no stage of acetylation is the hygroscopicity of the substituted jute higher than that of the unsubstituted one, the observed changes in the spacing and intensity of the reflections A_x and A_y cannot be due to absorption of moisture but are likely to be related to the introduction of the acetyl groups.

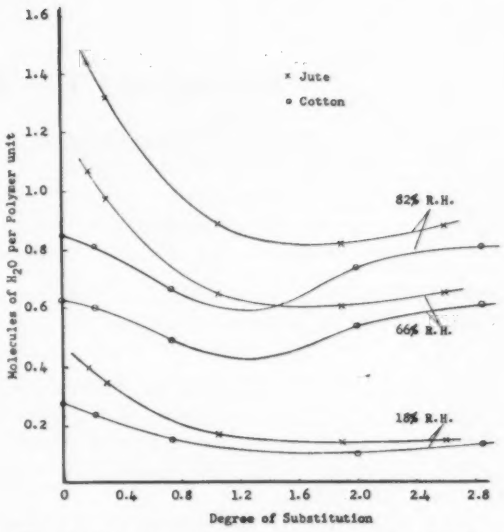

Fig. 3. Variation of moisture regain of acetylated jute and cotton (in glacial acetic acid medium) with degree of substitution.

The author wishes to thank Dr. W. G. Macmillan, Research Director, for permission to publish this note and Dr. M. K. Sen, Chief Physicist, for helpful discussion.

Literature Cited

1. Callow, H. J., *J. Textile Inst.* **43**, T423 (1952).
2. Gibbons, G. C., *J. Textile Inst.* **44**, T201 (1953).
3. Howsmon, J. A., "Cellulose and Cellulose Derivatives," Part I, Edited by E. Ott, H. M. Spurlin and M. W. Graffin, New York, Interscience Publishers Inc. 427 (1954).
4. Roy, S. C., TEXTILE RESEARCH JOURNAL **30**, 451 (1960).
5. Roy, S. C., *Proc. Technological Conf. ATIRA*, **A17** (Oct. 1959).
6. Sen, M. K. and Hermans, P. H., *Rec. Trav. Chim.* **68**, 1079 (1949).
7. Sen, M. K., *Science and Culture (India)* **16**, 440 (1950).
8. Sheppard, S. E. and Newsome, P. T., *J. Phys. Chem.* **33**, 1817 (1929).

S. C. Roy

Felting and Tip Weathering of Wool

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To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Investigations in this laboratory on the formation of non-woven wool felt have shown that a mutant Merino wool can be formed into felt when dry and that the weathering of the fiber tips is a cause of shrinkage during felting.

Felting Lustre Mutant Merino wool [3] is a comparatively crimp-free wool, and it was found that a strong, coarse-textured felt could be made from this wool under dry atmospheric conditions. The felting of a carded batt of this wool was also studied while it was immersed in *o*-dichlorobenzene and rubbed between two ground glass plates. As the immersion liquid has approximately the same refractive index as the wool and the glass, it was possible to observe the behavior of a small proportion of dyed fibers which had been included in the batt. It was observed that the fibers migrated only a few millimeters in the plane of the plates while consolidation of the batt thickness was taking place. The apparent absence of taut sections in any of the fibers suggested that no significant extension of the fibers was occurring, because the force required to exceed 3% extension of a wool fiber is several times that required to remove its crimp. It appears, therefore, that fiber extension is not an essential part of this felting process, although it probably does occur during the more severe industrial flat-hardening process, which produces more fiber migration.

During the rubbing, the batt shrank in area, although the only compressive force applied was perpendicular to the area. It was expected that under these conditions the batt would have spread rather than shrunk, because, while all the fibers in a batt are migrating, the batt may be regarded as a very viscous (compressible) fluid whose dimensions change slowly under the action of small forces. Thus, if the fibers migrate while the batt is compressed, they should rearrange themselves so that the batt yields and consolidates in the direction of the compression. A theory to explain the observed area shrinkage is that shrinkage occurs because the "root-end," i.e., the front end, of the fiber migrates faster through one region of the batt than the "tip-end" (rear) concurrently migrates through a second region. In the absence of fiber extension, the two regions would be drawn together at a rate equal to the difference in speed of the fiber through the two regions. If all the fibers behaved similarly there would be little tendency for fibers to stretch, as long as the felt density was low.

In order to measure and compare accurately the distance migrated by different fibers under identical conditions, a reference point in the felt, which was shrinking and which was composed of fibers migrating in all directions, was required. This problem was solved by forming a temporary composite of three fibers dyed different colors; two of them were the fibers to be compared, and they were arranged to migrate in the same direction, while the third was a synthetic protein fiber, Merinova, whose ends served as reference points to measure the distance moved by the corresponding ends of the other fibers. The composite was formed by holding the constituent fibers under sufficient tension to remove their crimp and bonding them together with water-soluble glue. When dry, the composite fiber was trimmed at each end and inserted in a batt of carded Merino wool. This was then placed in a flat-hardener, where the glue was washed out thoroughly with hot water, before proceeding with the flat-hardening in 2% sodium oleate solution at 70° C. The dyed fibers were examined after the felted batt had been washed, dried, and immersed in *o*-dichlorobenzene. A comparison of the speed of migration of sections 1½ in. long cut from the tip-ends of Merino fibers with sections cut from the root-ends (i.e., the ends of the fibers that were nearest to their roots before shearing) of the same fibers showed the root-end sections to move faster in all cases. See Figure 1. Measurements by Bradbury [1] have shown that the against-scale coefficient of friction was lower and the with-scale coefficient was higher at the weathered tip-ends than at the unweathered root-ends of the

Fig. 1. Wool fiber section r_1r_2 cut from the root-end has migrated about 30% further than the weathered tip-end section t_1t_2. The ends of the synthetic fiber m_1m_2 are the reference (starting) points.

fibers. The difference between the frictional coefficients was therefore greater in the case of the faster migrating fibers.

Bromine water has a shrinkproofing action similar to the action of chlorine, and measurements were made to compare the migration speed of bromine-treated and untreated mutant Merino fibers in the absence of water. This test was made using nitrocellulose cement to bond the test fibers, which were placed horizontally in a batt of mutant Merino wool. The batt was slightly flat-hardened before being soaked overnight in acetone to dissolve the cement. Results showed that the bromine water treatment reduced the migration speed and that the root-ends of the untreated fibers did in fact migrate further than their tip-ends, when the distances were measured from the corresponding ends of the Merinova reference fibers. The Merinova fibers became buckled as the batt shrank.

Small quantities of mutant Merino wool, all of which had been treated in bromine water over half the fiber length at the root-end, were hand carded and submitted to the normal amount of flat-hardening while dry. Instead of shrinking, the batt expanded in area without consolidating much in thickness, and the peripheral fibers were bowed in compression with very few fiber ends showing. This was because the rear ends of the fibers migrated faster past their neighbors than the (treated) front ends migrated past *their* neighbors, with the result that each migrating fiber tended to push the batt apart. On the other hand tip-end-treated wool shrank rapidly and the peripheral fibers radiated from the felted area, because, in this case, the local migration speed of the front ends was greater than that of the (treated) rear ends, with the result that each migrating fiber tended to gather the batt together. A mixture of equal quantities of tip-end-treated and root-end-treated wool felted much more quickly than untreated wool. This was because the root-end-treated fibers, that were tending to expand the batt, buckled in compression under a smaller force than that required to extend the tip-end-treated fibers. The shrinkage effect of the tip-end-treated fibers therefore predominated. These tests were repeated using wet batts, and the same results were obtained, except that there was more consolidation in all cases.

These results further support the unequal-migration-speed theory of shrinkage and offer an explanation of the results of Martin [2] who studied the wash shrinkage of fabric constructed from fibers having bromine-treated ends. Preliminary measurements of the distance migrated by mutant Merino compared with the normal crimped Merino have shown the uncrimped fibers to migrate at about six times the speed of the crimped fibers.

Acknowledgment

I wish to thank Dr. S. J. Leach and Mrs. K. R. Makinson for useful discussions.

Literature Cited

1. Bradbury, J. H., TEXTILE RESEARCH JOURNAL (in press).
2. Martin, A. J. P., *J. Soc. Dyers Colourists* **60**, 325–328 (1944).
3. Short, B. F., *Nature* **181**, 1414–1415 (1958).

G. F. FLANAGAN

Sandocryl Dye Staining as a Light Microscopical Technique for Acrylic Fibers

Central Research Laboratories
Toyo Rayon Co., Ltd.
Otsu, Japan
January 4, 1961

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

A group of synthetic fibers generically named acrylics seems to be highly interesting as a subject for microscopical investigation because of the diversity in their chemical, structural, and morphological properties.

Phase contrast microscope and a cross-sectional staining technique using basic dye are available for this purpose. The former allows unstained cross-section preparations to be examined in dark-to-bright contrast pictures, which reveal the internal structures in terms of the optical density. The dye-staining technique is more important not only in differentiating the internal features by means of the stainability against the basic dye employed but also in providing information which could be closely correlated with the practical dyeability of the fiber under observation.

It has been found that the Sandocryl dyeing process [1], which is a recently developed refinement of the cuprous-ion method for the dyeing of polyacrylonitrile fibers, can be adapted as a microscopical stain specific for acrylic fibers. A staining solution with the following composition is recommended.

Sandocryl Black NBLC-1	0.2%
$CuSO_4 \cdot 5H_2O$	0.2%
Copper wire mesh	5 g./l.

pH to be adjusted to 3 with phosphoric acid.

The slides carrying fiber cross sections are stained in the above solution at boil for about 30 min., then thoroughly rinsed with water and mounted as usual for examination.

It is rather well established that the Sandocryl dyeing on acrylic fibers depends upon the formation of a copper complex salt among cuprous ions produced in the dyebath and nitrile groups lying on the polymer chains, followed by the combination of the complex ion with the acid dye ion. The technique presented here, consequently, should be regarded as a kind of chemical stain peculiar to acrylic fibers. In fact, its specificity is found to be so high that most fibers other than acrylics are not stained a bit. Although some protein fibers, such as wool, may be dyed to a dark shade by the procedure, it is evident that Sandocryl Black dye behaves there only as an acid dye in acidic medium, for quite the same staining results are obtained when both copper sulfate and copper metal are removed from the dye solution described above. These components are essential in order for the Sandocryl dyeing of acrylic fibers to take place.

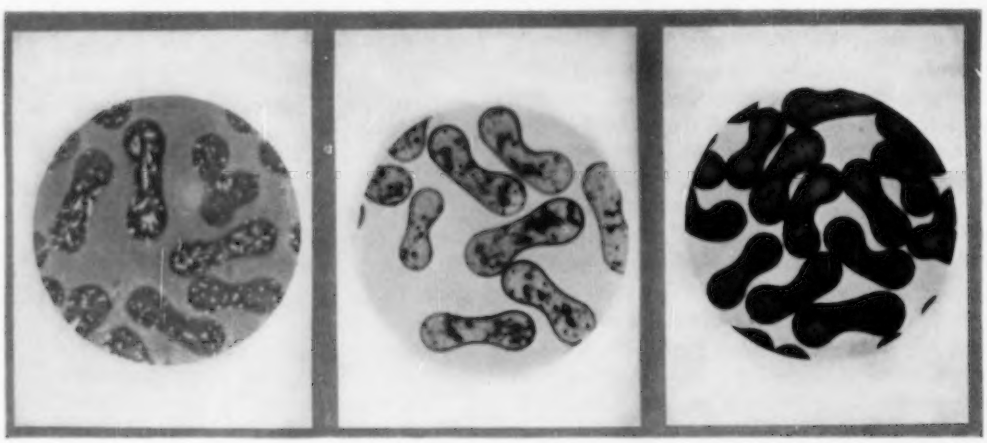

Fig. 1. Orlon (Du Pont acrylic fiber).

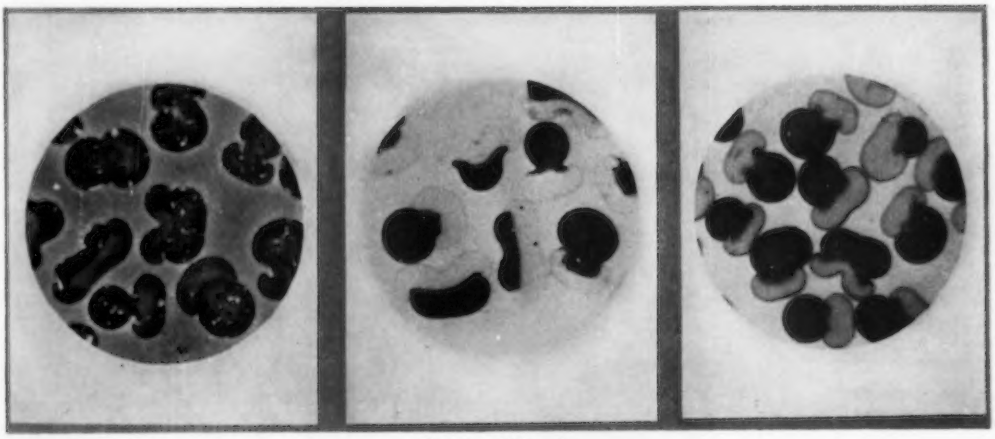

Fig. 2. Orlon 21.

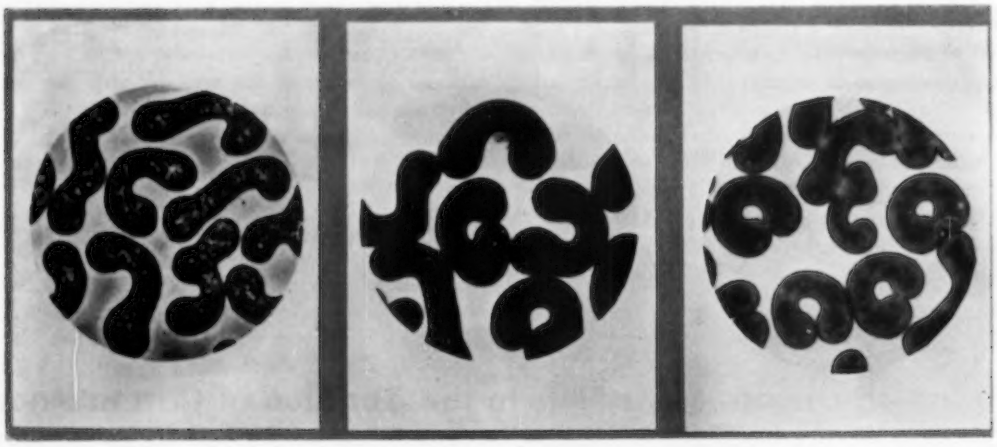

Fig. 3. Dynel.

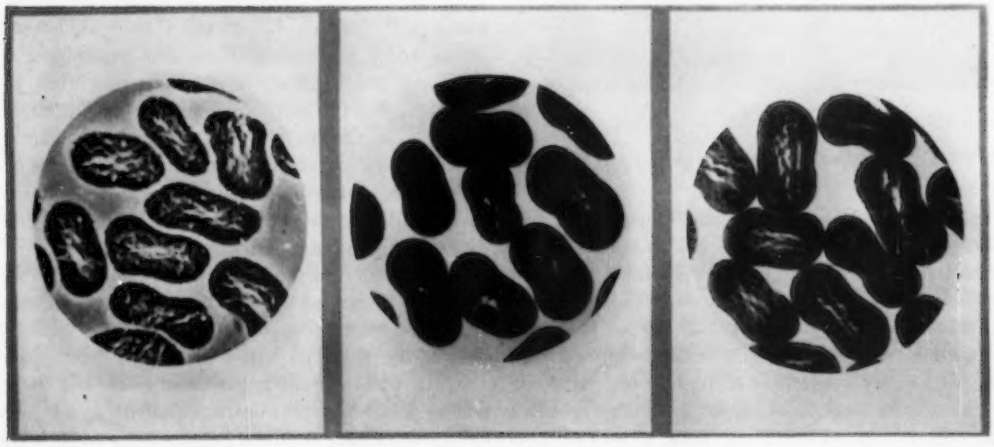

Fig. 4. Verel.

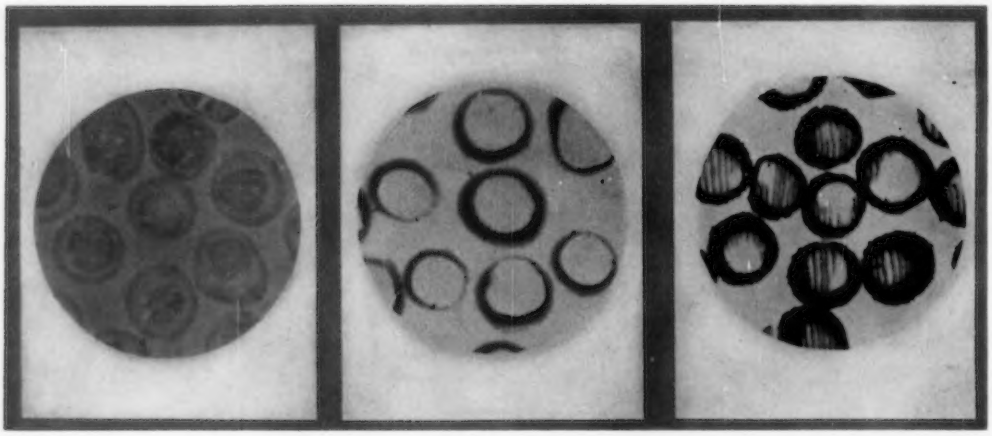

Fig. 5. Zefran.

Several results of a comparative study are illustrated in Figures 1 to 5, where each set of three photomicrographs is arranged in the same order from left to right: phase contrast picture, Victoria Blue staining, and Sandocryl Black staining. Canada balsam is being used as the common mountant and the magnification of micrographs also is fixed at 500 diameters throughout all figures.

It should be added that acrylonitrile polymer processed onto viscose rayon or other fibers can be detected in an excellent manner by the present procedure. Cellulose fiber, otherwise not stained at all, becomes also more or less stainable after the cyanoethylation processing using acrylonitrile.

Literature Cited

1. Schmitt, C. H. A., Saalfrank, C. W., and Walker, H. R., *Am. Dyestuff Reptr.* **44**, 904 (1955).

KOICHI KATO

A Note on Directional Effects in the Abrasion of Cotton Sateen

Textile, Clothing and Footwear Division
Quartermaster Research and Engineering Center
Natick, Massachusetts
January 16, 1961

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The considerable work that has been done in the field of abrasion resistance has led to certain generalizations regarding the behavior of fabrics of different weave types. In 1946 Kaswell [2] observed that "fabrics abraded in different directions have the same abrasion-resistance rank when tested in a single direction; fabrics abraded in a single direction show inverse abrasion-resistance when tested in perpendicular directions. The sateen back when abraded and tested warpwise, and the twill face when abraded and tested fillingwise, are the most abrasion-resisting surfaces." Morton [3] found that if abrasion and stress occur in opposite directions, maximum wear will take place when the non-stress bearing yarns are presented to the rubbing surface with their floats running in the direction of rubbing. Backer [1] mentions that advantage can be taken of this property by exposure of the face or back of the material to the rubbing element depending upon which side exposes the non-stressed yarns.

The U. S. Army has utilized these findings in its 8.5 oz./yd.^{2} carded sateen which is always worn with the filling flush side (back) of the fabric to the outside of the garment. In this system, the non-stress bearing (filling) yarns are first subjected to wear followed by the stress bearing (warp) yarns. Some recent tests have confirmed the validity of these early

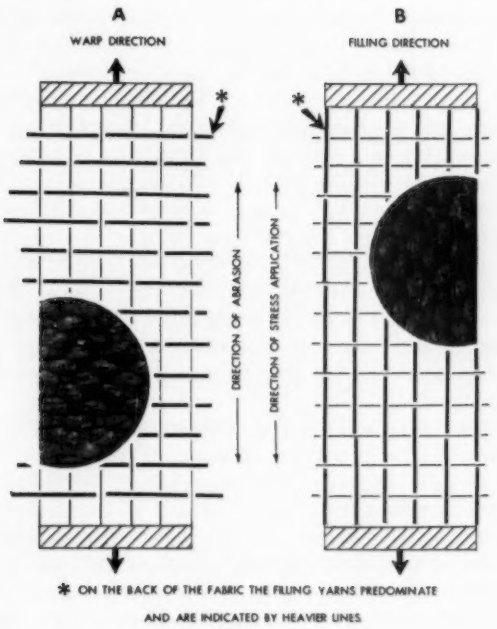

Fig. 1.

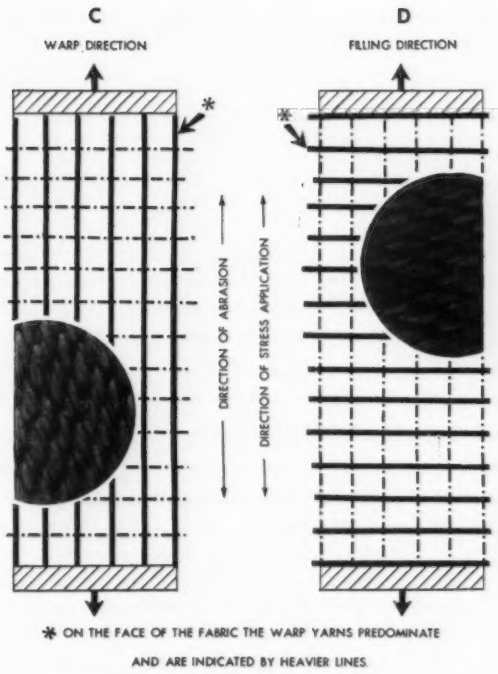

Fig. 2.

observations and have shown rather good agreement between warp direction abrasion on the back of sateen fabric and the filling direction on the face; and conversely between warp direction abrasion on the face and filling abrasion on the back. The accompanying sketches illustrate the location of the yarn systems with respect to the direction of abrasion; the relative positions of the stress bearing yarn system; and the yarn direction which is subjected to initial abrasive action. For example, in Figure 1 the fabric is shown with the back (filling flush) side to the abradant. As shown in the sketch on the left, the filling yarns are perpendicular to the direction of motion of the abradant whereas the warp yarns which are the stress bearing yarns in this particular system are parallel to the direction of motion of the abradant. Because of the nature of the sateen weave the filling yarns occupy a raised position on the back of the fabric and will be abraded first. In the particular abrading system used for these fabrics, namely the Stoll-QM Universal Abrader [4], 4 lb. of tension was applied to the stress bearing warp yarns. During the course of the test, the fibers from the filling yarns were broken and rolled into a small cylindrical mass which was periodically removed from the field of the abradant action. As abrasion continued, the

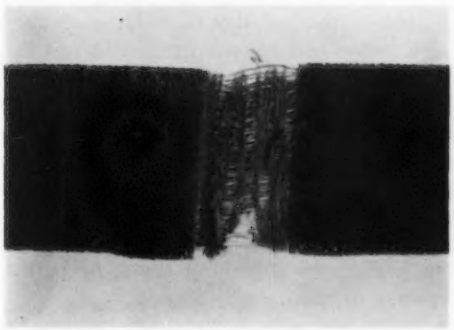

Fig. 3.

warp yarns began to appear through the filling yarn mass and as shown in Figure 3 it was possible to abrade away practically all of the filling yarns and still have the stress bearing warp yarns remain relatively intact. As the test continued the warp yarns were then abraded until rupture of the fabric occurred. Thus, it appears that the total abrasion resistance to rupture is equal to that of the filling yarns plus that of the warp yarns up to the point where the warp yarns had been decreased in breaking strength to 4 lb., which was the applied tension.

TABLE I. Number of Cycles to Rupture for Four Different Sateens, Abraded on Face and Back in Both Warp and Filling Directions

	Back		
	Warp	Filling	Difference
Sample 1	890	630	260
Sample 2	1530	930	600
Sample 3	2160	1200	960
Sample 4	970	670	300
	Face		
	Warp	Filling	Difference
Sample 1	530	810	−280
Sample 2	1000	1610	−610
Sample 3	1480	2220	−740
Sample 4	660	910	−250

In the sketch on the right of Figure 1, where the direction (parallel to filling yarns) of abrasion is 90° to that described above, the filling yarns again failed initially forming a similar small cylindrical mass of broken fibers. As the abrasive action continued to the point at which the filling yarns were destroyed, the warp yarns then came into play to contribute additional wear. However, since in this case the filling yarns were the stress bearing yarn system, the warp yarns could contribute nothing to support the 4 lb. of tension and accordingly when the filling yarns were abraded to the point where the filling yarn system had dropped in strength to 4 lb. the specimen ruptured. Thus, abrasion resistance in the filling direction on the back side of the fabric is contributed to only by the filling yarns themselves with the possible addition of the few interlacings of warp which appear on the back of the fabric. The difference between warp and filling direction abrasion on the back of sateens may range from approximately 300 to 1000 cycles depending upon the particular fabric being tested.

As shown in Figure 2, the same reasoning outlined above would be applicable. However, for the face of the fabric, filling-direction abrasion required the greater number of cycles to rupture. Actual data for four different sateens which were abraded on the face and the back in both the warp and filling directions are shown in Table I. The close correspondence for a given sample, between face-warp and back-filling and between face-filling and back-warp abrasion is noteworthy. In addition, the numerical differences for each sample, between the warp and filling directions for the back and the face of the sample show a rather good agreement. This would lead to the conclusion that each yarn system acts somewhat independently of the other. Furthermore, complete participation by both yarn systems can be obtained only when the stress bearing yarn system is "buried."

The simplicity of this mechanism suggests the possibility of predicting the abrasion resistance of a homogeneous group of materials in terms of parameters which may be closely related to the strength and mass of the stress bearing yarn system and the mass of the orthogonal system, which must literally be worn away before the stress bearing yarns can be brought into play to sustain the applied load. In addition, one may conclude that the proper placement of yarns in fabric types to bring about optimal covering and support by the stress bearing yarn system could lead to significant improvements in the wear resistance of our common textile fabrics.

Literature Cited

1. Backer, Stanley, "The Relationship Between the Structural Geometry of Textile Fabrics and Their Physical Properties, Part II. Abrasion Resistance." HQ, QM, R&E Command, Textiles Series Report No 61, September 1949.
2. Kaswell, E. R., TEXTILE RESEARCH JOURNAL **16**, 413 (1946).
3. Morton, W. E., *J. Textile Inst.* **39**, P187 (1948).
4. U. S. Government, Federal Specification CCC–T–191b (May 15, 1951), "Textile Test Methods," Method 5300.

LOUIS I. WEINER

Book Reviews

Manual of Man-Made Fibers. C. Z. Carroll-Porczynski. New York, Chemical Publishing Co., Inc., 1961. 304 pp. Price $10.

Reviewed by Dr. R. K. Toner, Editor, Textile Research Journal, Princeton, New Jersey

Part I of this manual is a classification of textile fiber products according to the Federal Trade Commission Identification Act of 1958. Part II covers natural polymer man-made fibers such as regenerated cellulose, cellulose ester, and regenerated protein fibers. Part III is concerned with the many synthetic polymer fibers: polyamides, polyesters, acrylic, polyolefines, etc. Part IV presents the inorganic fibers such as glass and mineral wool. Part V discusses textured yarns and Part VI presents information on the identification of fibers. Parts VII and VIII consist of a portfolio of photomicrographs and X-ray diffraction photographs of fibers, while Part IX is a very extensive bibliography (almost 40 pages). The book concludes with a list of man-made-fiber producers throughout the world and an index to the book.

Under each fiber is given a flow sheet for its manufacture and a table of properties, dyeing characteristics, electrical properties, and miscellaneous information. There are numerous graphs showing moisture regain and tensile behavior.

As indicated by the title, this book is a manual rather than a text book. As such it provides a single source where the reader may get, in condensed form, information about all the man-made fibers of current interest. The extensive bibliography permits one to extend this information to any extent he desires.

This volume should be in all reference libraries.

Viscoelastic Properties of Polymers. John D. Ferry. New York, John Wiley and Sons, Inc., 1961. vii, 482 pp. Price $15.00.

Reviewed by Arthur Tobolsky, Department of Chemistry, Princeton University, Princeton, New Jersey

This book is written by a distinguished contributor to the field of viscoelastic properties of polymers, and the quality of the book reflects the high quality of the author's research. Among the important topics covered are: the phenomenological theory for linear viscoelasticity, a discussion of experimental methods for viscoelastic measurements, a quite complete discussion of the results of the molecular theory for chain molecules, and applications to the behavior of specific systems. The book requires close study, but will be very useful to serious students of viscoelastic behavior. A useful feature is the wide range of references quoted and cited in the book. It is highly recommended.

Information for Contributors

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There are five principal classes of contributions suitable for the JOURNAL: (1) fundamental research articles, presenting important new information and data in any area of science related to the textile field; (2) technical papers describing development work, engineering advances, and innovations in manufacture and processing; (3) laboratory techniques with sufficient experimental data to illustrate the utility of methods or equipment described; (4) Letters to the Editor, seldom exceeding 1000 words, which are intended for prompt publication of new discoveries or observations, or for informative comment on papers previously published in the JOURNAL; (5) review articles of an authoritative and critical nature on a topic of major importance.

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Size of Original	Height of Letters
4 × 5	2–3 mm.
8 × 10	4–5 mm.
10 × 16	8+ mm.

Titles should not appear on the drawings; they will be set in type below the figures and should be submitted together on a separate sheet. Any legible reproduction of the figures may accompany the second copy of the manuscript.

Photographs—Photographs should be glossy prints, clear, sharp, and with as much contrast as possible without loss of detail. Identification of the figures should be made very lightly on the back with a soft pencil.

Literature Cited—All references cited in the text should be given in brackets, e.g., [2] by numerals corresponding to a numbered list, *arranged alphabetically by author,* at the end of the paper. The information should be given in the following order: authors' names, initials, name of publication, volume number, (place of publication and publisher for a book), inclusive page numbers, and year of publication. Abbreviations of journal titles follow those used by *Chemical Abstracts.*

In the July Issue

Dimensional Changes in Multicomponent Systems of Fabrics. A Theoretical Study. *Joel Lindberg*

Converting the Fibrograph to Automatic Direct-Reading Operation. *P. R. Ewald and Smith Worley, Jr.*

Graft Polymerization of Acrylamide onto Cotton Fabric for Further Treatments. *H. Kamogawa and T. Sekiya*

Isocyanate Modification of Wool in Dimethyl Sulfoxide. *N. H. Koenig*

Thermal Neutron Irradiation of Cotton. *Florine A. Blouin, Jett C. Arthur, Jr., Rollin S. Orr, and Vega J. Ott*

The Effect of Blending Cottons of Dissimilar Fiber Properties upon Spinning Performance and Yarn Quality. *William T. Waters and Joe Phillips*

The Supercontraction of Sound and Weathered Keratin Fibers. *O. A. Swanepoel*

Relaxation Shrinkage of Wool Fabrics: Its Release with Regain and Time. *K. Baird*

The Load–Extension Properties of Warp Knitted Fabrics. *D. L. Cook and P. Grosberg*

Measurement of the Modulus of Dynamic Elasticity of Staple Fibers. *H. G. Weyland*

The Molecular Structure and Mechanical Properties of Polyethylene Terephthalate Fibers. *I. M. Ward*